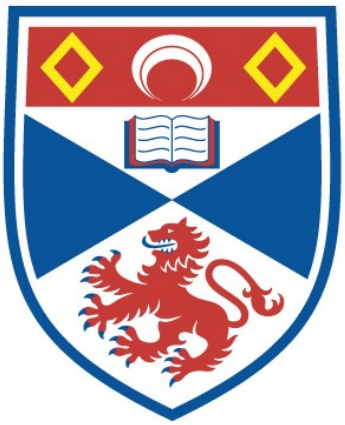
NEW REAGENTS AND SYNTHESES IN HETEROCYCLIC ORGANOSELENIUM CHEMISTRY

Richard Allan Speirs

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1986

New Reagents and Syntheses

in Heterocyclic Organoselenium Chemistry

being a Thesis presented by

Richard Allan Speirs, B.Sc.

to the

University of St. Andrews,

in application for

the Degree of Doctor of Philosophy

To my parents

Declaration

I, Richard A. Speirs, hereby certify that this thesis has been composed by myself, that it is a record of my own work, and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

16th December 1985

Signed Date

I was admitted to the Faculty of Science of the University of St. Andrews under Ordinance General No. 12 on 1st October 1982, and as a candidate for the Degree of Ph.D. on 1st October 1983.

16th December 1985

Signed Date

I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate to the Degree of Ph.D..

26 November 1985

Signature of Supervisor Date

12 December 1985

Signature of Supervisor Date

University Career

I entered the University of St. Andrews in October 1978, and subsequently graduated with Upper Second Class Honours in Chemistry in July 1982.

In October 1982 I was awarded a Purdie Research Grant by the University of St. Andrews, and from then until September 1985, I carried out the work which is embodied in this thesis. This work was undertaken in the Department of Chemistry, University of St. Andrews, initially under the supervision of Professor D. H. Reid, and latterly under the joint supervision of both Professor D. H. Reid and Dr R. K. Mackie.

Acknowledgements

I should like to express my gratitude to Professor D. H. Reid and to Dr R. K. Mackie for their advice, guidance and interest in my work.

I should also like to thank Professor Lord Tedder and Professor P. A. H. Wyatt for making available the laboratory facilities in the Department of Chemistry, University of St. Andrews. My thanks are also due to the technical staff for their invaluable assistance.

Furthermore, I am indebted to Miss C. H. Finlay, Mr P. J. Pogorzelec, Mrs W. A. Pogorzelec, and Mr N. M. Speirs for their help in preparing the typescript of this thesis.

Finally, I should like to thank the University of St. Andrews for the award of a Purdie Research Grant.

Explanatory Note

This thesis is divided into three sections Parts A, B and C. These parts are further divided into a number of principal sections prefixed by a Roman numeral.

Part A consists of review of the relevant background literature, Part B consists of a discussion of the experimental results obtained and Part C is complementary to Part B and comprises the experimental details of the results discussed in Part B.

Reference made to the chemical literature is indicated by a number in superscript, a key to which can be found in the bibliography in Appendix 4.

The structural formulae which have been reproduced for illustrative purposes have been assigned Arabic numerals corresponding to those which have been given to the relevant compounds in the text.

CONTENTS

PART A: INTRODUCTION

	PAGE
1. The Introduction Of Selenium Into Organic Compounds	1
A. Inorganic Reagents	3
1) Elemental Selenium	3
2) Hydrogen Selenide And Alkali Selenides	8
3) Potassium Selenocyanate And Related Compounds	14
4) Phosphorus(V) Selenide	18
5) Selenium Dioxide, Selenious Acid And Selenium Trioxide	22
6) General Nucleophilic Selenium Reagents	26
7) Selenium Halides And Oxyhalides	31
B. Simple Organic Reagents	36
1) Selenourea	36
2) Benzylselenol	36
3) Carbon Diselenide	38
2. The Introduction Of Sulphur Into Carbonyl Compounds Using Organothiophosphorus Reagents	40
A. Phosphorus Thioacids And Their Derivatives	41
1) Phosphorus Dithioacids	41
2) S-Trimethylsilyl Esters Of Phosphorus Dithioacids	43
3) Thiophosphates And Thiophosphoric Diamides	44
4) Phosphine Sulphides	45

PAGE

B. Lawesson's Reagent 46

1) Reactions With Ketones 46

2) Reactions With Esters Of (Thio)Carboxylic Acids 49

3) Reactions With Amides Of Carboxylic Acids 49

3. 1,6,6aλ^4-Triheterapentalenes Containing Selenium 52

A. Structural Studies 53

1) X-Ray Crystallography 53

2) Nuclear Magnetic Resonance Spectroscopy 60

3) Miscellaneous Spectroscopic Techniques 63

B. Bonding 65

C. Synthesis Of Selenium 1,6,6aλ^4-Triheterapentalenes And Related Systems 68

1) From Dioximes And Bis-hydrazones 68

2) From 4H-(Thio)Pyran-4-selones 69

3) From 3-Alkyl-1,2-diselenolium Salts 70

4) From Other 1,6,6aλ^4-Triheterapentalenes 72

D. Reactions Of Selenium 1,6,6aλ^4-Triheterapentalenes And Related Systems 73

1) Protonation Of 1,6-Dioxa-6aλ^4-selenapentalenes 73

PAGE

4. Indolizine-3-carboselenaldehydes 75

A. Structural Studies 76

1) Nuclear Magnetic Resonance Spectroscopy 76

2) Miscellaneous Spectroscopic Techniques 77

B. Bonding 78

C. Synthesis Of Indolizine-3-carboselenaldehydes 79

D. Reactions Of Indolizine-3-carboselenaldehydes 80

PAGE

PART B: DISCUSSION

1. Synthesis Of Selenium-Transfer Reagents 81

A. Synthesis Of Phenylphosphonoselenoic Dichloride 81

B. Synthesis Of Diphenylphosphonoselenoic Chloride 83

C. Synthesis Of Tetramethylammonium Selenocyanate And Its Reaction With Dichlorophenylphosphine 84

2. Preparation Of Carbonyl Compounds 88

A. Preparation Of (1,2-Dithiol-3-ylidene)carbaldehydes 88

B. Preparation Of Indolizine-3-carbaldehydes 89

1) Preparation Of Pyridinium Bromide Salts 89

2) Preparation Of Indolizines 90

3) Preparation Of Indolizine-3-carbaldehydes 91

3. Reactions Involving Selenium-Transfer Reagents 94

A. Synthesis Of 1,6aλ^4-Dithia-6-selenapentalenes 94

B. Synthesis Of Indolizine-3-carboselenaldehydes 99

C. Synthesis Of Pentacarbonyl(indolizine-3-carboselenaldehyde-Se)tungsten(0) Complexes 107

PAGE

D. Synthesis Of Miscellaneous Selenocarbonyl Compounds 113

1) Synthesis Of N,N-Dimethylselenoformamide 113

2) Synthesis Of 5-Phenyl-3H-1,2-dithiole-3-selone 115

3) Synthesis Of 2,6-Dimethyl-4H-pyran-4-selone 117

4) Attempted Synthesis Of 4(1H)-Pyridineselone 118

5) Attempted Synthesis Of 1-Methylpyrrolidine-2-selone 119

6) Attempted Synthesis Of Hexahydro-2H-azepine-2-selone 120

7) Attempted Synthesis Of 2,4,6-Cycloheptatriene-1-selone 120

E. Synthesis Of Miscellaneous Pentacarbonyl(selone-Se)-tungsten(0) Complexes 122

1) Attempted Synthesis Of Pentacarbonyl(2,6-dimethyl-4H-pyran-4-selone-Se)tungsten(0) 122

2) Synthesis Of Pentacarbonyl(2,4,6-cycloheptatriene-1-selone-Se)tungsten(0) 123

F. Reaction Of Indolizine-3-carbaldehydes With The Reagent Formed By The Reaction Of Phenyldichlorophosphine With Tetramethylammonium Selenocyanate 126

PAGE

PART C: EXPERIMENTAL

Introductory Notes 135

1. Synthesis Of Selenium-Transfer Reagents 142

A. Synthesis Of Phenylphosphonoselenoic Dichloride 142

B. Synthesis Of Diphenylphosphonoselenoic Chloride 143

C. Synthesis Of Tetramethylammonium Selenocyanate 144

2. Preparation Of Carbonyl Compounds 146

A. Preparation Of (1,2-Dithiol-3-ylidene)carbaldehydes 146

B. Preparation Of Indolizine-3-carbaldehydes 146

1) Preparation Of Pyridinium Bromide Salts 146

1-(3,3-Dimethyl-2-oxobutyl)-2,3-dimethylpyridinium Bromide 146

1-(3,3-Dimethyl-2-oxobutyl)-5,6-dihydro-5H-1-pyrindinium Bromide 147

1-(3,3-Dimethyl-2-oxobutyl)-5,6,7,8-tetrahydro-quinolinium Bromide 148

1-(3,3-Dimethyl-2-oxobutyl)-6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridinium Bromide 149

2) Preparation Of Indolizines 150

2-t-Butyl-8-methylindolizine 150

1-t-Butyl-7,8-dihydrocyclopent[hi]indolizine 151

1-t-Butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]quinoline 151

1-t-Butyl-7,8,9,10-tetrahydrocyclohept[hi]indolizine 152

PAGE

3) Preparation Of Indolizine-3-carbaldehydes 153

2-t-Butyl-7-methylindolizine-3-carbaldehyde 153

2-t-Butyl-1-methylindolizine-3-carbaldehyde 154

2-t-Butyl-8-methylindolizine-3-carbaldehyde 155

1-t-Butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]-quinoline-2-carbaldehyde 157

1-t-Butyl-7,8,9,10-tetrahydrocyclohept[hi]-indolizine-2-carbaldehyde 158

3. Reactions Involving Selenium-Transfer Reagents 160

A. Synthesis Of 1,6aλ^4-Dithia-6-selenapentalenes 160

2-Phenyl-1,6aλ^4-dithia-6-selenapentalene 160

2-t-Butyl-1,6aλ^4-dithia-6-selenapentalene 162

2-Phenyl-4-methyl-1,6aλ^4-dithia-6-selenapentalene 163

4,5-Dihydro-3H-[1,2]thiaselenolo[4,5,1-hi][1,2]-benzodithiole-7a-S^4 164

B. Synthesis Of Indolizine-3-carboselenaldehydes 167

2,7-Dimethylindolizine-3-carboselenaldehyde 167

2-t-Butyl-7-methylindolizine-3-carboselenaldehyde 168

2-t-Butyl-1-methylindolizine-3-carboselenaldehyde 169

2-t-Butyl-8-methylindolizine-3-carboselenaldehyde 171

1-t-Butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]quinoline-2-carboselenaldehyde 173

1-t-Butyl-7,8,9,10-tetrahydrocyclohept[hi]indolizine-2-carboselenaldehyde 174

PAGE

C. Synthesis Of Pentacarbonyl(indolizine-3-carboselenaldehyde-Se)tungsten(0) Complexes 176

Pentacarbonyl(2,7-dimethylindolizine-3-carboselenaldehyde-Se)tungsten(0) 176

Pentacarbonyl(2-t-butyl-7-methylindolizine-3-carboselenaldehyde-Se)tungsten(0) 177

Pentacarbonyl(2-t-butyl-1-methylindolizine-3-carboselenaldehyde-Se)tungsten(0) 179

Pentacarbonyl(2-t-butyl-8-methylindolizine-3-carboselenaldehyde-Se)tungsten(0) 180

Pentacarbonyl(1-t-butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]quinoline-2-carboselenaldehyde-Se)tungsten(0) 182

Pentacarbonyl(1,2-dimethylindolizine-3-carboselenaldehyde-Se)tungsten(0) 183

D. Attempted Synthesis Of Miscellaneous Selenocarbonyl Compounds 185

N,N-Dimethylselenoformamide 185

5-Phenyl-3H-1,2-dithiole-3-selone 186

2,6-Dimethyl-4H-pyran-4-selone 188

4(1H)-pyridineselone 189

1-Methylpyrrolidine-2-selone 190

Hexahydro-2H-azepine-2-selone 191

2,4,6-Cycloheptatriene-1-selone 192

PAGE

E. Attempted Synthesis Of Miscellaneous Pentacarbonyl-(selone-Se)tungsten(0) Complexes 193

Pentacarbonyl(2,6-dimethyl-4H-pyran-4-selone-Se)-tungsten(0) 193

Pentacarbonyl(2,4,6-cycloheptatriene-1-selone-Se)-tungsten(0) 194

F. Reaction Of Indolizine-3-carbaldehydes With The Reagent Formed By The Reaction Of Phenyldichlorophosphine With Tetramethylammonium Selenocyanate 196

Reaction With 2,7-Dimethylindolizine-3-carbaldehyde 196

Reaction With 2-t-Butyl-7-methylindolizine-3-carbaldehyde 198

Reaction With 2-t-Butyl-1-methylindolizine-3-carbaldehyde 200

Reaction With 2-t-Butyl-8-methylindolizine-3-carbaldehyde 202

Reaction With 1-t-Butyl-8,9-dihydro-7H-pyrrolo-[3,2,1-ij]quinoline-2-carbaldehyde 204

Reaction With 1,2-Dimethylindolizine-3-carbaldehyde 206

PAGE

APPENDIX 1: ^{1}H N.m.r. Spectral Data 209

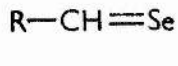
APPENDIX 2: ^{13}C N.m.r. Spectral Data 228

APPENDIX 3: Mass Spectral Data 241

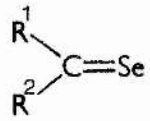
APPENDIX 4: Bibliography 249

Abstract

The main aim of this project was to develop new reagents capable of exchanging selenium for oxygen under mild conditions, to obtain new carboselenaldehyde (1) and selone (2) compounds.

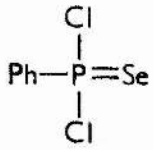


(1)

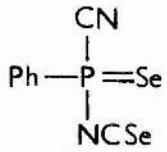


(2)

Two such reagents are phosphorus compounds (3) and (4).

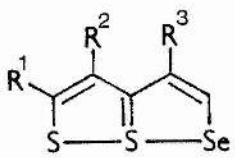


(3)

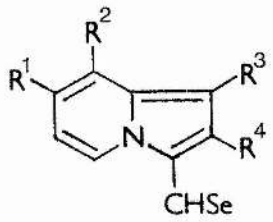


(4)

Phenylphosphonoselenoic dichloride (3) was prepared as a solution in xylene. It was reacted with (1,2-dithiol-3-ylidene)carbaldehydes and indolizine-3-carbaldehydes to afford 1,6aλ^4-dithia-6-selena-pentalenes (5) and indolizine-3-carboselenaldehydes (6), respectively. The indolizine-3-carbaldehydes had previously been prepared from the corresponding indolizines, in turn prepared from the appropriate pyridinium bromide salts.

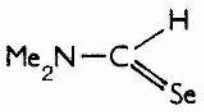


(5)

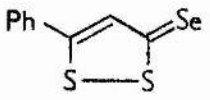


(6)

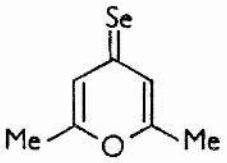
Phenylphosphonoselenoic dichloride (3) was also reacted with several other carbonyl compounds. Reactions with N,N-dimethylformamide, 5-phenyl-3H-1,2-dithiol-3-one, 2,6-dimethyl-4H-pyran-4-one, 4-hydroxypyridine, 1-methylpyrrolidin-2-one, hexahydro-2H-azepin-2-one, and 2,4,6-cycloheptatrien-1-one met with varied success, and only N,N-dimethylselenoformamide (7), 5-phenyl-3H-1,2-dithiole-3-selone (8), and 2,6-dimethyl-4H-pyran-4-selone (9) were obtained.



(7)

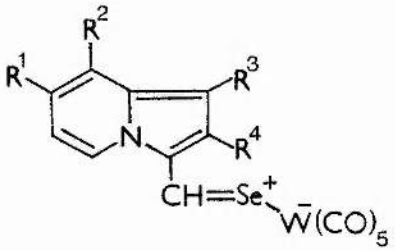


(8)

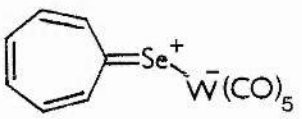


(9)

The presence of a stabilising substituent was therefore required, and was introduced as a tungsten pentacarbonyl species. Pentacarbonyl(indolizine-3-carboselenaldehyde-Se)tungsten(0) (10) and pentacarbonyl(2,4,6-cycloheptatriene-1-selone-Se)tungsten(0) (11) were obtained from the reaction of the corresponding carbonyl compounds with phenylphosphonoselenoic dichloride (3) in the presence of tetraethylammonium iodopentacarbonyltungstate(0).



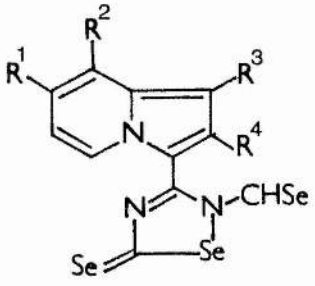
(10)



(11)

The reagent (4) was prepared from the reaction of chlorodiphenylphosphine and tetramethylammonium selenocyanate, and was reacted *in situ* with indolizine-3-carbaldehydes to produce not only indolizine-

3-carboselenaldehydes (6), but also compounds which were proposed on the strength of spectral and analytical evidence as being members of the novel 3-(indolizin-3-yl)-2,5-dihydro-2-selenoformyl-1,2,4-selenadiazole-5-selone (12) system.



(12)

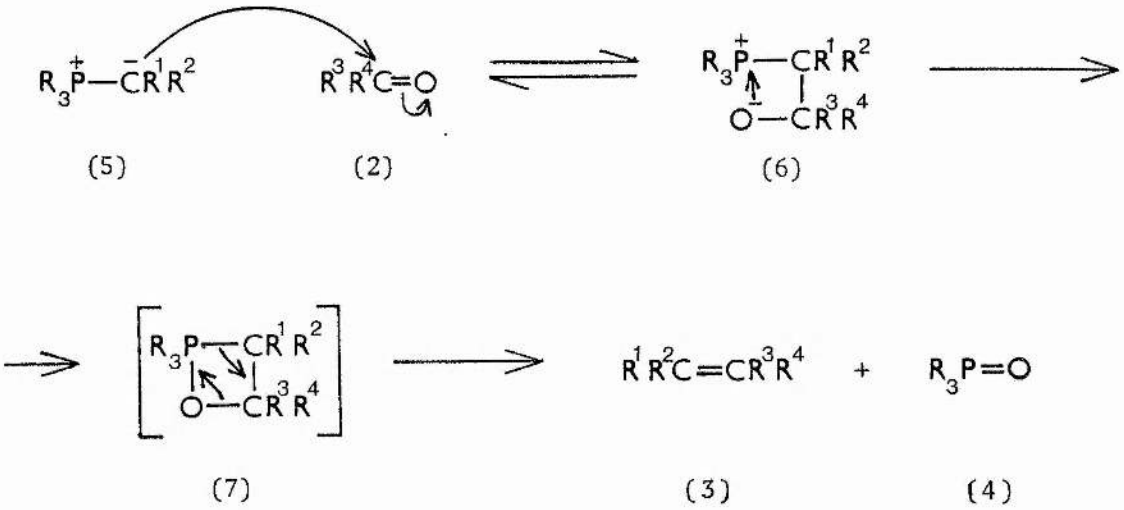
Foreword

The aim of the work described in this thesis was to develop new reagents for effecting the exchange of selenium for oxygen under mild conditions, in order to form a selone or carboselenaldehyde function, or to insert selenium into a heteroaromatic ring structure. It was proposed initially that phosphine selenide compounds be reacted with carbonyl, or masked carbonyl, groups to achieve this end. Since it was postulated that this exchange might be brought about in a reaction involving a four-centre cyclic intermediate similar to that in the Wittig reaction, a brief discussion of the Wittig reaction is appropriate.

The Wittig reaction is a condensation/elimination reaction between a phosphonium ylide (1) and a compound (2) containing an aldehydic or ketonic function. The products are an alkene (3), and a phosphine oxide (4). The reaction has been extensively reviewed[1-11], and the ground-state of the phosphonium ylide is known to have a considerable contribution from the charged structure (5).

$$\underset{(1)}{R_3P{=}CR^1R^2} \rightleftharpoons \underset{(5)}{R_3\overset{+}{P}{-}\overset{-}{C}R^1R^2} \xrightarrow[(2)]{R^3R^4C{=}O} \underset{(3)}{R^1R^2C{=}CR^3R^4} + \underset{(4)}{R_3P{=}O}$$

In the accepted mechanism of the Wittig reaction, the electrophilic carbonyl carbon atom undergoes attack by the nucleophilic ylide carbon atom to form a betaine intermediate (6). This intermediate may then give rise to the expected alkene (3), and phosphine oxide (4), products via a cyclic, four-centre transition state (7).



(5) (2) (6)

(7) (3) (4)

It is now generally accepted that the formation of the phosphorus-oxygen bond in the phosphine oxide (4) presents a most favourable contribution to the energy profile. It is this energetically favourable driving-force that is utilised in the exchange reactions described in this thesis.

PART A

INTRODUCTION

1. The Introduction Of Selenium Into Organic Compounds

Since the work described in this thesis concerns the exchange of selenium for oxygen in organic compounds, and the reagents that will bring about this under mild conditions, it is appropriate to discuss the reagents and methods that have been previously used in order to achieve the insertion of selenium into organic molecules. The advantages and disadvantages of the various methods will be explained where appropriate, so that it may be appreciated that there is scope for new reagents that will bring about this introduction of selenium under milder and more advantageous conditions, thereby minimising the loss of any of the products due to decomposition.

The field of organoselenium chemistry, although expanding, is still relatively small, and organoselenium compounds are relatively scarce compared with the number of analogous oxygen, or even sulphur, compounds. However, the preparation, and to a lesser extent reactions, of organoselenium compounds have been reviewed[12-21]. One point that emerges is that the smaller weight compounds, especially heterocyclic compounds, often possess relatively low thermal stability when compared with their sulphur and oxygen analogues, and are more reactive towards light and oxygen. This makes their preparation considerably less straight forward, and comparatively mild and often darkened, occasionally even inert, reaction conditions are necessary. Many of the reagents that have previously been used to insert selenium into organic compounds, and which are referred to in the following discussion, employ reaction conditions that preclude these requirements.

The reagents that are discussed here may be classified as being

either inorganic or organic, the former being more prevalent.

A. Inorganic Reagents

1) Elemental Selenium

a) Thermal Reactions

Reactions of this type, having been developed in the late 19th Century, represent one of the oldest methods of introducing selenium into organic compounds. Selenium is commonly obtained as a grey powder, although due to the rather insoluble nature of selenium, the use of the more finely divided 'red' allotrope is preferable. Unfortunately, the 'red' allotrope tends to change into the more stable grey form under the influence of heat and light. Selenium powder may also be contaminated with traces of sulphur or tellurium, and these impurities can be very difficult to remove, especially once present in organic molecules. In addition, elemental selenium does not always appear to be as reactive as sulphur in comparable reactions, often being recoverable after the reaction. However, examples of reactions utilising selenium in one-step processes are well known.

One such reaction type is the preparation of aromatic mono-selenides (1) from symmetrical diarylsulphones (2)[22-24].

$$\underset{(2)}{Ar_2SO_2} + Se_x \xrightarrow{\Delta} \underset{(1)}{Ar_2Se} + SO_2$$

There are disadvantages however. The first is that relatively high reaction temperatures, up to 300°C, are required, and sulphur dioxide gas is produced as a by-product. The main disadvantage however, is that the reaction does not necessarily cease with the

preparation of the monoselenides. Further selenium atoms may be inserted to produce not only the diselenides (3), but also polyselenides (4)[23].

$$\underset{(1)}{Ar_2Se} + Se_x \xrightarrow{\Delta} \underset{(3)}{Ar_2Se_2} + \underset{(4)}{Ar_2Se_n}$$

This produces separation and purification problems, especially since polyselenides (4) liberate elemental selenium comparatively easily when heated even gently, or when in contact with oxidising or reducing agents, or even in the presence of solvents, as might be the case during separation. A further inconvenience is that these reactions are of relatively limited use, for if unsymmetrical sulphones or monoselenides are used[25], then the number of products increases, making separation even more difficult.

Different problems are encountered when diaryl mercury compounds (5) are reacted with selenium, although single products are obtained in each case. When temperatures in excess of 200°C are used, diaryl selenides (1) are obtained[26-29].

$$\underset{(5)}{Ar_2Hg} + Se_x \xrightarrow{\Delta} \underset{(1)}{Ar_2Se} + Hg$$

Although these reactions afford excellent yields, the presence of mercury, and mercury compounds is undesirable. However, provided the diaryl mercury compounds (5) are available, this procedure is very useful. Of rather more limited use, are the reactions to produce diselenides from mercury compounds. When the mercury salts of tri-

fluoroacetic acid (6) and difluoroacetic acid (7) are heated in the presence of selenium, hexafluorodimethyldiselenide (8)[30] and tetrafluorodimethyldiselenide (9)[31] are afforded respectively.

$$(CF_3CO_2)_2Hg + Se_x \xrightarrow{\Delta} (CF_3)_2Se_2$$

(6) (8)

$$(CHF_2CO_2)_2Hg + Se_x \xrightarrow{\Delta} (CHF_2)_2Se_2$$

(7) (9)

Selenium may also react with certain compounds so as to be present in the ring of a cyclic product. It will insert into the thiacyclobutane ring of compound (10) to form the 1-thia-2-selenacyclopentane ring of compound (11)[32] in good yield. However, potassium cyanide is required as a catalyst, and vigorous reaction conditions are necessary.

(10) (11)

(12) (13)

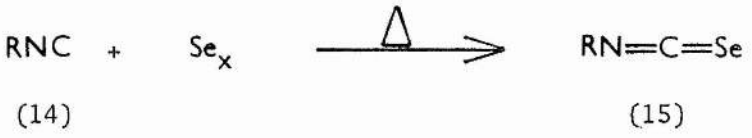
Selenium will also react with 2,3-diiodohexafluorobut-2-ene (12) to form tetrakis(trifluoromethyl)-1,4-diselenin (13)[33], although in

poor yield.

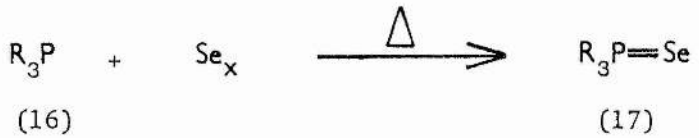
In conclusion, thermal reactions incorporating selenium into organic compounds are complicated by handling and purification problems, and require relatively drastic reaction temperatures.

b) Addition Under Mild Conditions

Two main types of compound are observed to undergo reaction with elemental selenium under mild conditions to afford selenium-containing products in excellent yields. Isonitriles (14) react with selenium in solution at temperatures less than 100°C to give isoselenocyanates (15)[34-37], and trivalent phosphorus derivatives (16) afford substituted phosphine selenides (17)[16].



(14) (15)



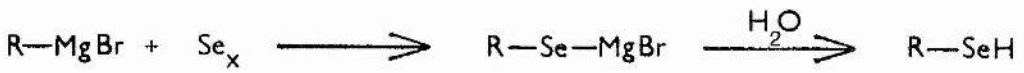
(16) (17)

Both reactions are general, and are of great importance in the preparation of selenoureas, selenosemicarbazides and organoselenium heterocycles, and of phosphine selenides and selenophosphates respectively.

c) Addition To Organometallic Reagents

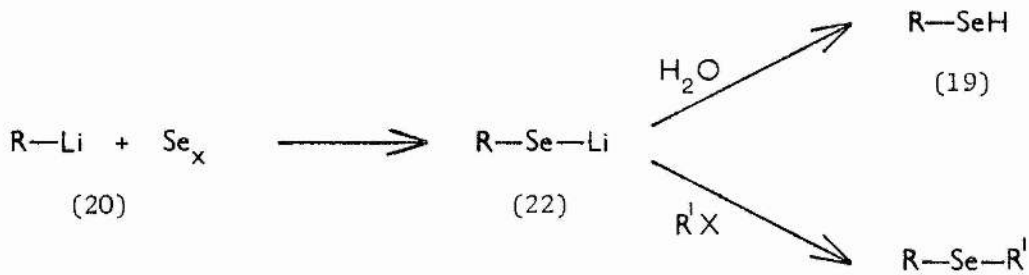
Organometallic reagents that possess a potential carbanion will react vigorously with dry selenium in relatively polar solvents at

room temperature to form metal salts of the corresponding selenols. Since aliphatic selenium derivatives may often be obtained directly from the corresponding halides by nucleophilic substitution, the use of Grignard reagents (18) is normally restricted to reactions affording aromatic selenium derivatives such as selenols (19)[38-43]; cf. Section 1.B.2).



(18) (19)

In a convenient general route, organolithium reagents (20) react with selenium to give selenols (19) or selenol derivatives (21) via the lithium salts (22) of the selenols[44-46].



(20) (22) (19) (21)

Alkali-metal acetylides (23) react with selenium in liquid ammonia to form alkali alkynyl selenides (24)[47-50].

(23) (24) (25)

These selenides (24) are then usually alkylated to acetylenic

selenides (25) due to the instability of the alkynyl selenides (24).

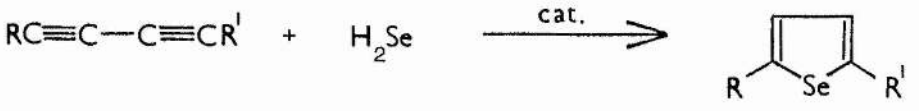
These reactions take place vigorously at ambient or even lower temperatures, and dry reagents are necessary. The usefulness of elemental selenium to bring about the introduction of selenium into organic compounds is therefore variable, and is often accompanied by handling problems.

2) Hydrogen Selenide And Alkali Selenides

Hydrogen selenide is a colourless gas at room temperature, having a penetrating disagreeable odour, and is extremely toxic. It is readily oxidised in air and must therefore be handled in an inert atmosphere. It is also quite soluble in water, giving rise to a relatively strong acid, and is soluble in most organic solvents. It may be prepared directly from its elements at relatively high temperatures, or else from the hydrolysis of aluminium selenide in water or aqueous acid.

a) Addition To Multiple Bonds

A number of selenium-containing compounds have been formed by the addition of hydrogen selenide to suitably activated carbon-carbon double bonds[51,52], but these are not very common.



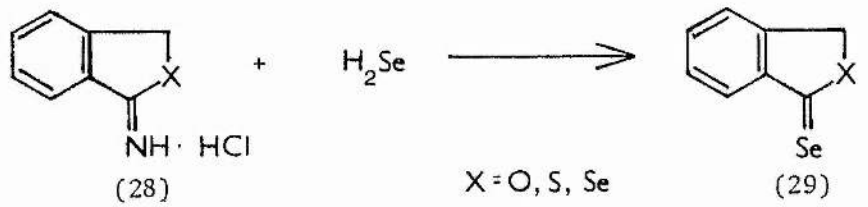
(27) (26)

One such example is the apparently general route to selenophenes

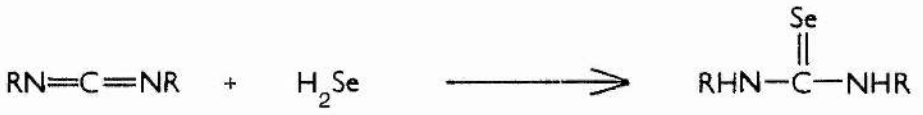
(26) from conjugated diacetylenes (27)[53].

Hydrogen selenide will also react with carbon-nitrogen double and triple bonds. The reaction with imino functions under mild conditions will produce selenocarbonyl groups, as in the reaction of the imino-ester hydrochlorides (28) to give 2-selenophthalide and related analogues (29)[54].

Aliphatic and aromatic carbodiimides (30) react very smoothly with hydrogen selenide to afford symmetrically disubstituted selenoureas (31)[55,56].



(28) (29)



(30) (31)

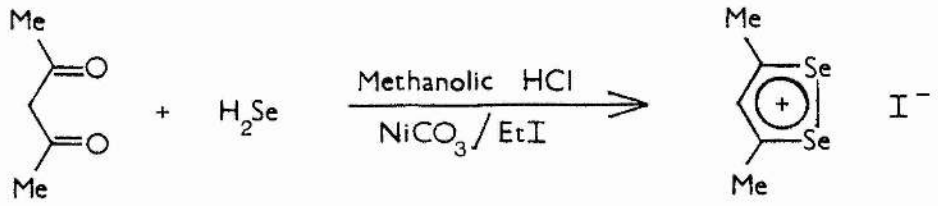
Similarly, the reaction between hydrogen selenide and the carbon-nitrogen triple bond appears to be quite general. Addition to nitriles (32) affords selenoamides (33)[57-61], as demonstrated by the reaction of cyanamide (34) and hydrogen selenide to produce selenourea (35)[62-64]. Alkyl cyanates (36) afford alkoxy selenocarbamates (37) when reacted with hydrogen selenide[65].

(32) (33)

(34) (35)

(36) (37)

Finally, hydrogen selenide will react with aliphatic carbonyl functions under a variety of conditions, usually reductively, to form diselenides[66]. The direct replacement of selenium for oxygen has been observed when acetylacetone (38) is allowed to react with hydrogen selenide in the presence of acids to afford the corresponding 1,2-diselenolium cation (39)[67]. This work was later modified and extended by Jackson to give variously substituted 1,2-diselenolium cations with various associated anions[68].



(38) (39)

b) Displacement Reactions

A few reactions have been observed where hydrogen selenide or alkali selenides react with small-ring compounds to effect heteroatom displacement and ring-opening[69]. The products are usually either the corresponding selenide or, due to the relative susceptibility of the first-formed selenols to oxidation, the diselenide. In addition, hydrogen selenide will react with aliphatic halides to afford selenides, or diselenides resulting from the oxidation of the first-formed selenols.

Usually these reactions involve the separate generation of hydrogen selenide, but this is not always necessary. Dialkyl selenides (21) and diselenides (40) may be obtained from the direct reaction of selenium with sodium in liquid ammonia to form either disodium monoselenide (41) or diselenide (42), depending upon the stoichiometry of the selenium and sodium employed, followed by alkylation[70,71].

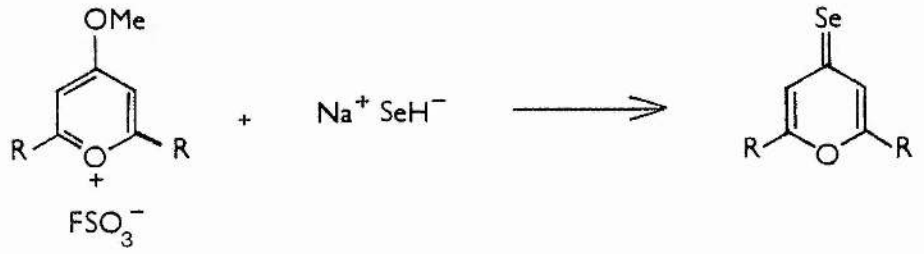
$$Se_x + 2\ Na \xrightarrow{\text{liq. } NH_3} \underset{(41)}{Na_2Se} \xrightarrow{R'X} \underset{(21)}{R{-}Se{-}R'}$$

$$2\ Se_x + 2\ Na \xrightarrow{\text{liq. } NH_3} \underset{(42)}{Na_2Se_2} \xrightarrow{R'X} \underset{(40)}{R{-}Se{-}Se{-}R'}$$

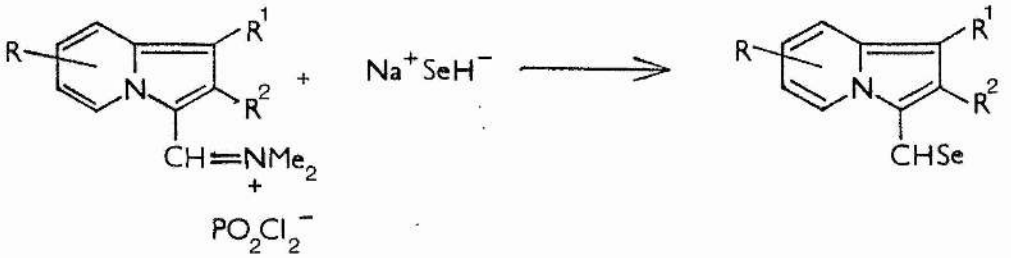
Sodium hydrogen selenide is often employed as an alternative reagent to hydrogen selenide, and is obtained by the vigorous reaction

of selenium with sodium borohydride, in either ethanolic or aqueous solutions[72]. Ethanolic sodium hydrogen selenide may be used for the synthesis of selenides, selenoureas and selenols, whilst aqueous sodium hydrogen selenide is a convenient reagent for forming the selenocarbonyl function.

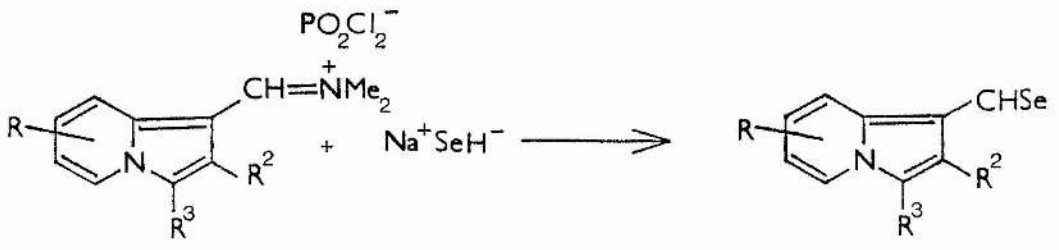
Thus, pyrylium fluorosulphonates (43) react with aqueous sodium hydrogen selenide to provide pyran-4-selones (44)[73], and the Vilsmeier salts (45), (46), (47) and (48) afford[74] indolizine-3-carboselenaldehydes (49), indolizine-1-carboselenaldehydes (50), pyrrolo[2,1-b]-thiazole-5-carboselenaldehydes (51) and pyrrolo[2,1-b]thiazole-7-carboselenaldehydes (52) respectively.



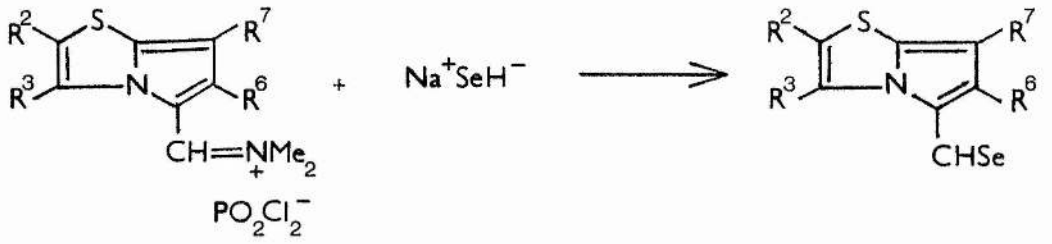
(43) (44)



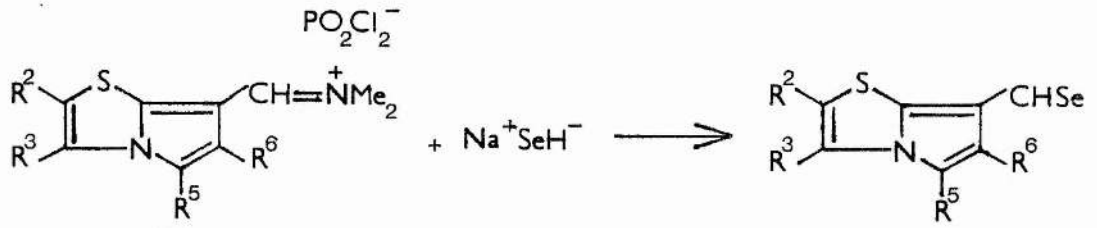
(45) (49)



(46) (50)

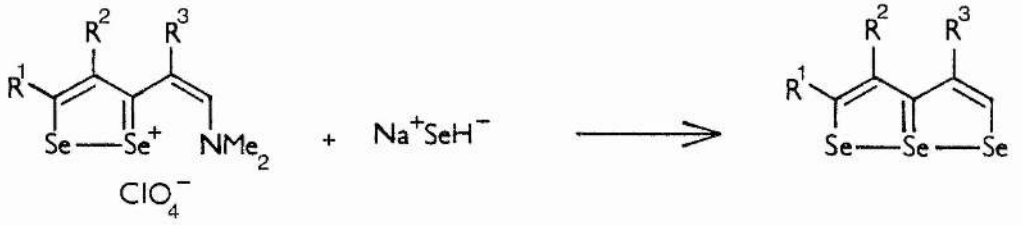


(47) (51)

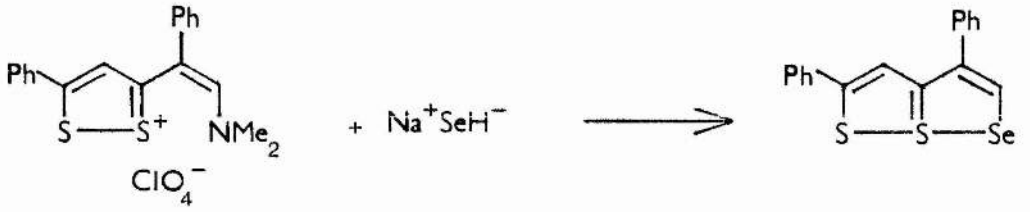


(48) (52)

Finally, the Vilsmeier salts (53) and (54) react with aqueous sodium hydrogen selenide to produce the 1,6,6aλ^4-triselenapentalenes (55)[68] and the 1,6aλ^4-dithia-6-selenapentalene (56) respectively[75].



(53) (55)



(54) (56)

In conclusion therefore, reaction yields with hydrogen selenide and alkali selenides are generally satisfactory to good, but the toxicity of hydrogen selenide must always be guarded against.

3) Potassium Selenocyanate And Related Compounds

Potassium selenocyanate is one of the best established reagents for the introduction of selenium into organic compounds. It may be readily obtained from selenium and potassium cyanide, either by direct fusion[76,77] or in refluxing ethanol[78]. Although it is very hygroscopic and slowly decomposes when in contact with a damp acidic environment, it is quite stable when kept dry. An advantage in its use is that it is soluble in solvents such as water, alcohols, N,N-dimethylformamide and acetonitrile, and so may be handled easily.

a) Nucleophilic Displacement Reactions

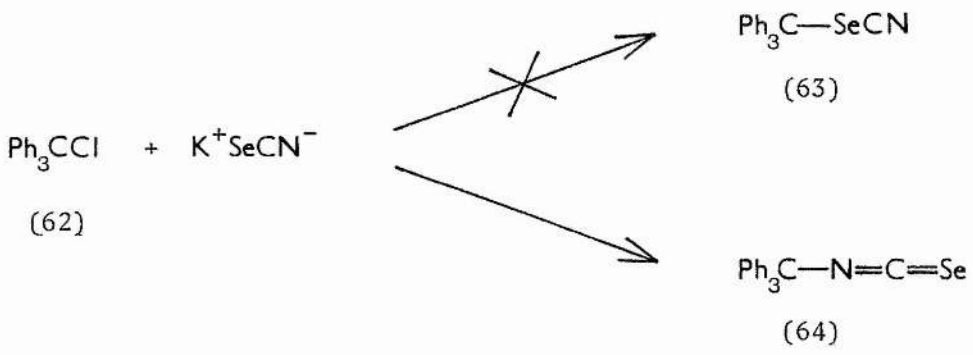
The nucleophilicity of the selenocyanate anion towards aliphatic halides and aromatic diazonium salts ensures the widespread use of this reagent. The progress of the reaction between potassium selenocyanate and an aliphatic halide (57) in refluxing alcohol to afford an aliphatic selenocyanate (58) may be monitored by the formation of potassium halide (59). The reaction with an aromatic diazonium salt (60) is usually carried out in an aqueous solution that is buffered to pH 5.5 or above, and the reagent is added dropwise to the diazonium salt (60) to form the aromatic selenocyanate (61). In this case, not only the formation of potassium halide (59), but also the evolution of nitrogen gas may be used to monitor the progress of the reaction.

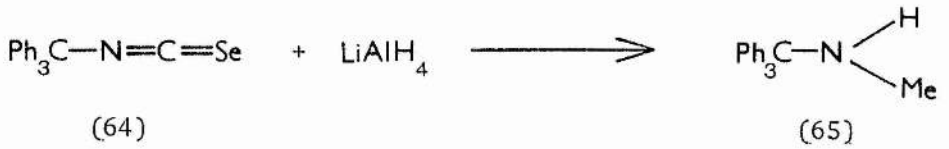
$$\underset{(57)}{RX} + K^+SeCN^- \longrightarrow \underset{(58)}{RSeCN} + \underset{(59)}{KX}$$

$$\underset{(60)}{ArN_2^+ X^-} + K^+SeCN^- \xrightarrow{pH \geq 5 \cdot 5} \underset{(61)}{ArSeCN} + \underset{(59)}{KX} + N_2$$

Although potassium selenocyanate will often produce the corresponding organic selenocyanate, it may also produce the isoselenocyanate, for the selenocyanate anion is known to be ambidentate and may react at either the selenium or nitrogen atom.

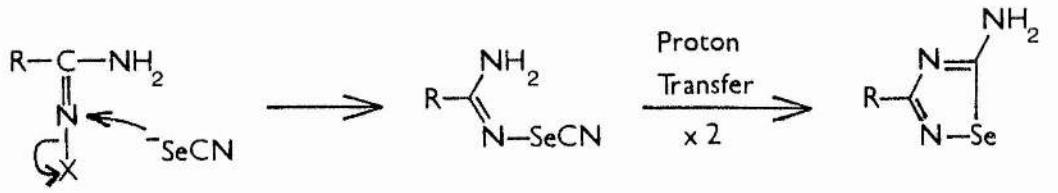
The reaction between triphenylmethyl chloride (62) and potassium selenocyanate was originally thought to have produced the triphenylmethyl selenocyanate (63)[79]. However, this was later shown not to be the case. Instead, the triphenylmethyl isoselenocyanate (64) had been produced, as indicated by infra-red spectroscopy, and by the fact that reduction with lithium aluminium hydride gave N-methyl-triphenylmethylamine (65)[80]. The compound could only have been obtained if the reactant was an isoselenocyanate compound, and not a selenocyanate.





Once a selenocyanate product has been produced, further reaction

may take place, as for the case when N-haloamidines (66) react with potassium selenocyanate to give the 3-substituted-5-amino-1,2,4-selenadiazoles (67)[81].



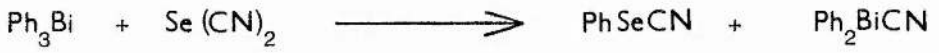
(66) (67)

b) Electrophilic Substitution Reactions

Via Dicyanodiselenide And Related Compounds

Three derivatives of potassium selenocyanate will participate in electrophilic substitution reactions; namely selenium dicyanide (68), dicyanodiselenide (69) and dicyanotriselenide (70).

Selenium dicyanide (68) is known to undergo reaction with triphenylbismuthine (71) to afford phenylselenocyanate (72) and diphenylcyanobismuthine (73)[82], but this appears to be an isolated reaction, and hence selenium dicyanide is not a practical reagent for the introduction of selenium into organic compounds.



(71) (68) (72) (73)

Dicyanotriselenide (70), which may be obtained by the oxidation of potassium selenocyanate with either chlorine, or with nitrogen dioxide and nitric acid[78], reacts with organic compounds, such as anilines (74)[82,83]. Reaction proceeds at ambient temperature to

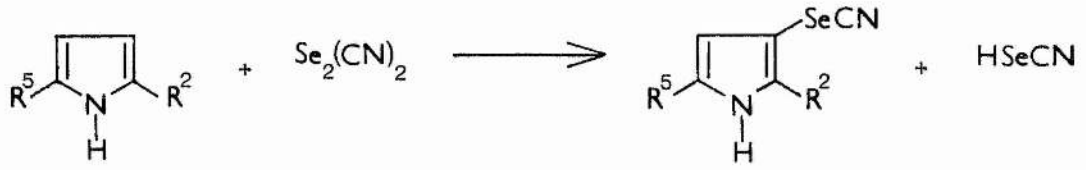
produce 4-selenocyanoanilines (75), selenocyanic acid (76) and selenium. Unfortunately, selenocyanic acid (76) is very unstable, and readily decomposes to afford selenium and toxic hydrogen cyanide gas (77). Lengthy reaction times are required, and overall yields are poor, so the use of dicyanotriselenide to introduce selenium is not of great practical use.

(74) (70) (75) (76)

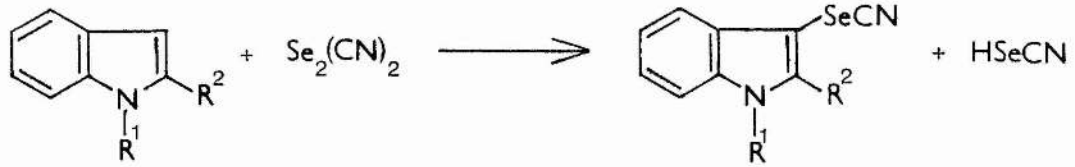
(76) (77)

Dicyanodiselenide (69) is much more useful. This reagent is prepared from potassium selenocyanate, by oxidation with lead tetra-acetate[84] or with bromine in methanol at -60°C[85]. The latter is more convenient, since the reagent may be used <u>in situ</u>. Electrophilic substitution reactions have been effected for many compounds using dicyanodiselenide. At -50°C, substituted anilines (74) yield the corresponding 4-selenocyanoanilines (75)[86], pyrroles (78) yield the corresponding 3-selenocyanopyrroles (79)[87], and indoles (80) give 3-selenocyanoindoles (81)[88,89]. Yields are reported to be generally good, making this reagent relatively useful for the introduction of selenium into organic molecules.

(74) (69) (75) (76)



(78) (69) (79) (76)



(80) (69) (81) (76)

In conclusion therefore, both potassium selenocyanate and dicyanodiselenide (69) are useful general reagents, although the former is more easily handled.

4) Phosphorus(V) Selenide

Phosphorus(V) selenide appears to be much less reactive towards organic compounds than phosphorus(V) sulphide. This extremely insoluble, dark-coloured solid is prepared directly from its elements by heating them in a dry, inert atmosphere in an enclosed vessel[90]. It is difficult to assess the purity of the product due to its amorphous and insoluble nature. Phosphorus(V) selenide is hydrolysed

by atmospheric moisture to hydrogen selenide and selenium, and like phosphorus(V) sulphide, it should therefore be stored in a dry, inert atmosphere.

a) Reactions With Alcohols

Several authors have investigated the reaction of phosphorus(V) selenide with various aliphatic and aromatic alcohols[90-95]. The expected dialkyldiselenophosphoric acids proved to be unstable, and so derivatives were usually isolated as the potassium salts of O,O'-dialkyldiselenophosphates. Side products were also obtained in these reactions, hindering isolation and purification.

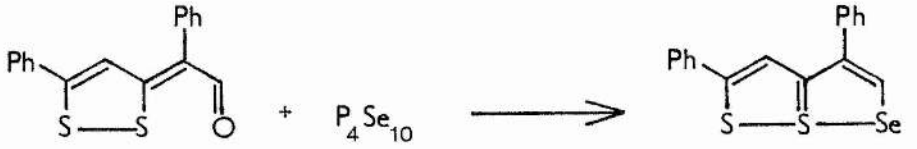
b) Reactions With Ammonia And Amines

The reaction of phosphorus(V) selenide with liquid ammonia has been reported to afford several products, the relative amounts of which depend upon the stoichiometric quantities of the reactants, and upon the reaction temperature[96]. Reactions of primary amines with this reagent afforded various selenophosphoric amides[97]. Due to the instability of these compounds, reactions had to be carried out in dry, inert atmospheres.

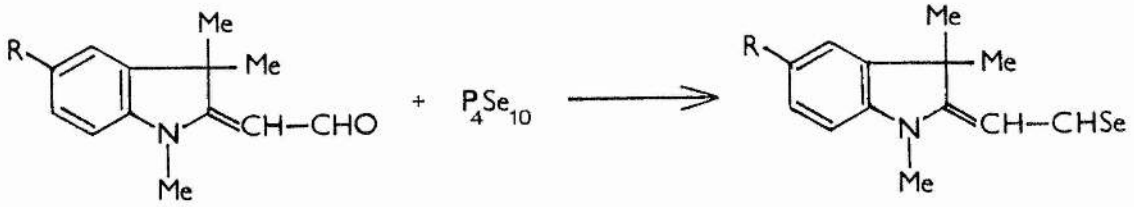
c) Reactions With (Thio)Carbonyl Functions

There are relatively few reported reactions between phosphorus(V) selenides and compounds containing carbonyl groups. Compound (82) reacts with phosphorus(V) selenide to afford an apparently quantitative amount of 2,4-diphenyl-1,6aλ^4-dithia-6-selenapentalene (56)[98]. In work reported in a patent, the indole derivatives (83) are said to afford the corresponding carboselenaldehyde compounds (84)[99].

Unfortunately, a systematic study of this type of reaction has not yet been undertaken to decide whether these reactions are of a general nature or not.



(82) (56)



(83) (84)

The reaction of formamide (85) and phosphorus(V) selenide to form selenoformamide (86) has recently been announced[100]. Other amides (87) have also yielded the corresponding selenoamides (88)[101-103], whilst tetraalkylureas (89) have afforded tetraalkylselenoureas (90)[104].

(85) (86)

(87) (88)

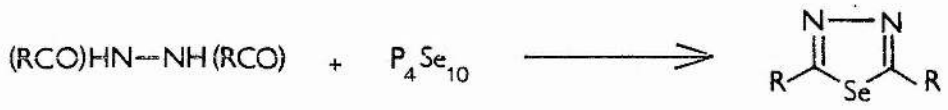
(89) (90)

These compounds tend to be unstable, and have to be stored in a dry, inert atmosphere, and in the dark.

The conversion of lactams (91) to selenolactams (92) by phosphorus(V) selenide, which was prepared and reacted *in situ*, has been reported[105]. The reaction times tended to be lengthy and the yields generally low, except for the case where n = 11, when a 40% yield of pure selenolactam was obtained.

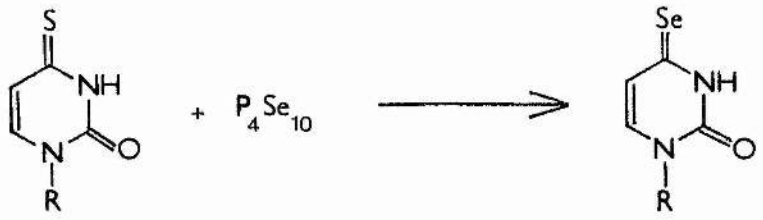
(91) (92)

1,3,4-Selenadiazoles (93) have been reported to be the product of the reaction of dialkyl- and diarylhydrazides (94) with phosphorus(V) selenide[106].



(94) (93)

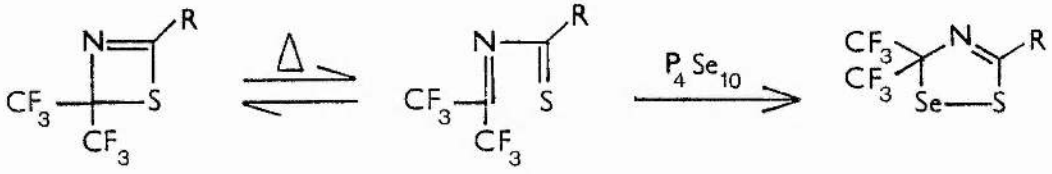
Finally, in the reaction of 1-alkyl-4-thiouracils (95) with phosphorus(V) selenide, the sulphur atom was replaced preferentially, since the observed products were 1-alkyl-4-selenouracils (96)[107].



(95) (96)

d) Miscellaneous Reactions

A report has appeared recently of the insertion of selenium into a heterocyclic ring using phosphorus(V) selenide[108]. Compound (97) exists in equilibrium with structure (98), and this equilibrium may be displaced towards compound (98) by heating. Subsequent reaction with phosphorus(V) selenide then afforded the heterocycle (99). However, this reaction is of very limited use.



(97) (98) (99)

In conclusion, the main drawback to the use of phosphorus(V) selenide is principally its very low solubility, and the relative instability of most of the products obtained. Reaction yields are generally low, reaction times lengthy, and purification complicated. Phosphorus(V) selenide is therefore a far from ideal reagent for effecting the insertion of selenium into organic compounds.

5) Selenium Dioxide, Selenious Acid And Selenium Trioxide

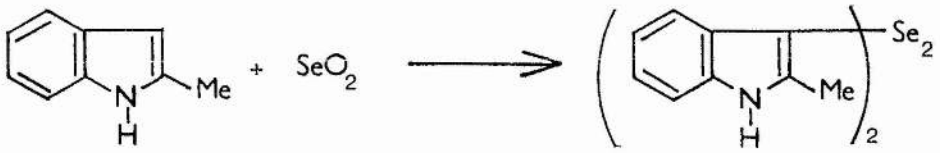
Many oxidation reactions involving selenium dioxide and its

hydrate, selenious acid, have been reported. Most of this work was not really concerned with the insertion of selenium into organic compounds, but rather the organic derivatives that do not contain selenium. Much less use has been made of these reagents for the insertion of selenium into organic molecules.

a) Reactions Involving $Se^{(IV)}$

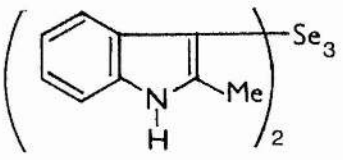
The reaction of indoles with selenium dioxide has been observed to be somewhat variable[109]. Indole (100) affords 3,3'-diindolylselenide (101), 2-methylindole (102) affords both 3,3'-di(2-methylindolyl)diselenide (103) and the corresponding triselenide (104), whilst 1,2-dimethylindole (105) affords 3,3'-di(1,2-dimethylindolyl)-triselenide (106). This variation in the type of product obtained, coupled with the relatively modest yields, suggests that there is little likelihood of this becoming a general reaction.

(100) (101)



(102) (103)

+

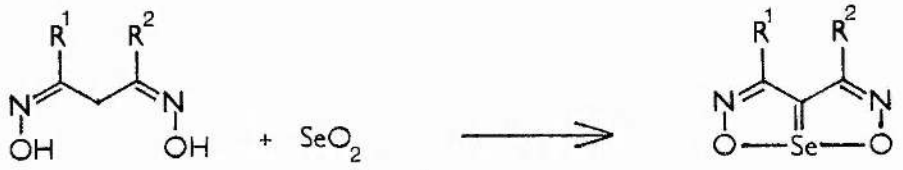


(104)

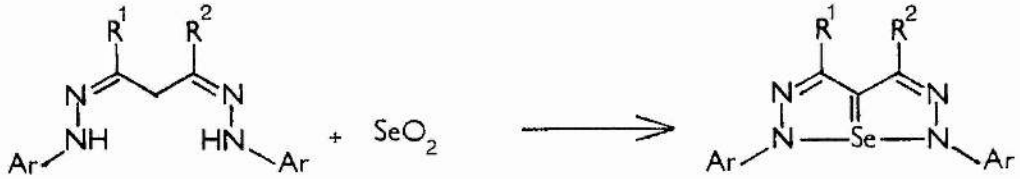
(105) (106)

Another type of reaction is that involving olefins and selenium dioxide under acidic conditions to introduce an allylic substituent, often with rearrangement[110-112]. However, compounds which do not contain selenium are usually formed, and so this type of reaction is not especially relevant in this context.

A number of heterocyclic compounds may be prepared using these reagents. Dioximes (107) and bis-hydrazones (108) react with selenium dioxide to afford 1,6-dioxa-6aλ^4-selena-2,5-diazapentalenes (109)[113-116] and 6aλ^4-selena-1,2,5,6-tetraazapentalenes (110)[114,117] respectively. The preparation of tetraazapentalenes (110) by this method is rather restricted in its applicability, since the aryl group must be either a phenyl or a 2,4-dinitrophenyl substituent.



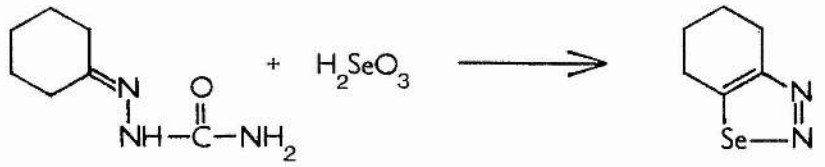
(107) (109)



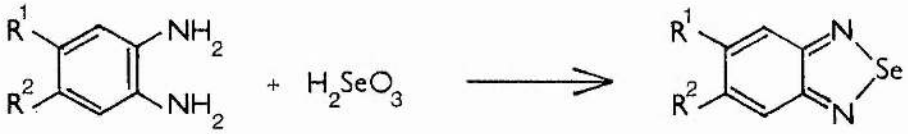
(108) (110)

Ar = C_6H_5 . 2,4-$(NO_2)_2$-C_6H_3

Benzoselenadiazoles may be prepared using selenious acid. The semicarbazone (111) affords 4,5,6,7-tetrahydro-1,2,3-benzoselenadiazole (112) under quite mild conditions[118], whilst in a general reaction, virtually quantitative yields of substituted 1,2,5-benzoselenadiazoles (113) may be obtained from the aromatic diamines (114)[119,120].



(111) (112)



(114) (113)

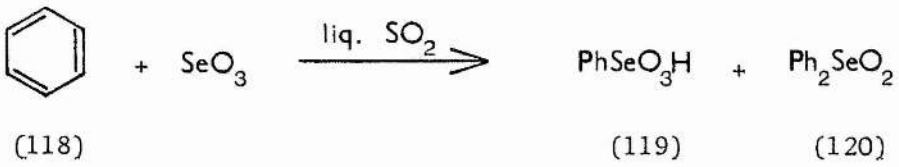
Selenious acid also reacts with thiols (115) in another general reaction to give dithioselenides (116) and disulphides (117)[121,122], but it is often very difficult to separate these products.

(115) (116) (117)

b) Reactions Involving $Se^{(VI)}$

Relatively little work has been carried out on electrophilic substitution reactions involving selenium trioxide. It has been

observed however, that benzene (118) reacts smoothly with a solution of selenium trioxide in liquid sulphur dioxide to afford a selenonic acid (119) as the main product, and a selenone (120) as a minor product[123]. The yield of the former may be decreased, and that of the latter increased, if a mixture of selenium trioxide in selenic acid, H_2SeO_4, is used instead of that in liquid sulphur dioxide. Bromobenzene and chlorobenzene react in an analogous manner.



(118) (119) (120)

Since relatively little work has been undertaken using these reagents as a means of inserting selenium into organic molecules, the above reactions would indicate that there might be scope in this area in the future.

6) General Nucleophilic Selenium Reagents

The reagents discussed in the following Section all contain highly nucleophilic selenium anions, capable of attacking carbon, displacing alkyl halide substituents, and ring-opening small heterocycles. They are all prepared directly from selenium, and are often used *in situ* rather than being isolated prior to use. They tend to be used in aqueous solutions under mild conditions and usually give good results. These reagents constitute a very useful means of forming new carbon-selenium bonds.

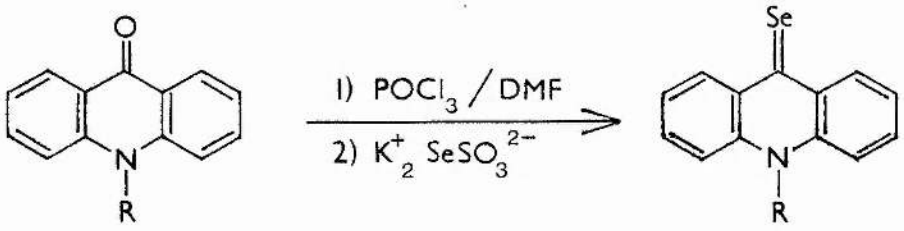
a) Potassium Selenosulphate

Potassium selenosulphate is readily prepared by dissolving selenium in an aqueous solution of potassium sulphite at 80°-100°C, and is used in preference to sodium selenosulphate since sodium sulphite is comparatively insoluble. Potassium selenosulphate is non-reducing, and also non-toxic. It may be isolated as an easily handled solid[124], or it may be used *in situ*[125]. It has been noted that when an aqueous solution of potassium selenosulphate is prepared, elemental selenium is deposited, as indicated by the following equilibrium[126].

$$SeSO_3^{2-} + H_2O \rightleftharpoons Se_x + HSO_3^- + OH^-$$

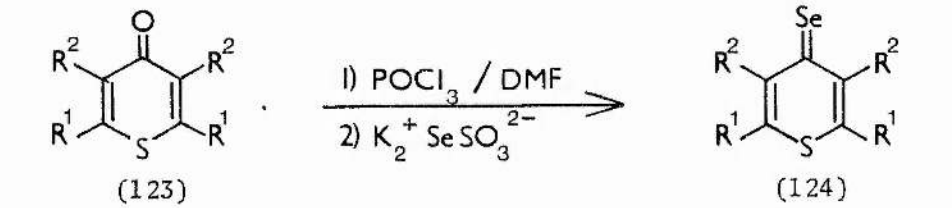
However, if the solution is kept at approximately 65°C, then the equilibrium favours the selenosulphate anion and there is less deposition of selenium, and consequently, a greater concentration of selenosulphate anions available for reaction.

Despite the lack of reducing ability, the selenosulphate anion is still sufficiently nucleophilic to effect substitution reactions. Treatment of the acridone (121) with phosphoryl chloride and N,N-dimethylformamide gives the corresponding chloro salt, which reacts with aqueous potassium selenosulphate to give the selenoacridone (122)[127].

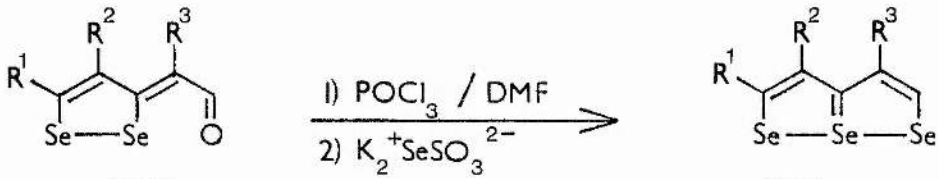


(121) (122)

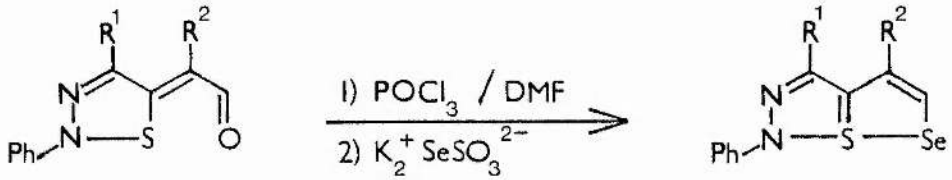
More recent work employing the same reaction conditions has converted the thiapyran-4-one (123) to the thiapyran-4-selone (124)[126], and the aldehydes (125) and (126) to 1,6,6aλ^4-triselenapentalenes (55)[68] and 6-selena-6aλ^4-thia-1,2-diazapentalenes (127)[128] respectively.



(123) (124)



(125) (55)



(126) (127)

This reagent therefore provides an efficient and relatively safe means of inserting selenium into organic compounds.

b) Selenide Anions

When elemental selenium is allowed to react with an aqueous solution of either sodium or potassium hydroxide, a solution containing highly reactive selenide anions is obtained. However, it has not proved possible to assign definite stoichiometric values to these anions, although Se_n^{2-} has been postulated[129,130]. If such solutions are reacted in situ with alkyl halides, various polyselenides are produced, corresponding to the appropriate selenide anions[12]. The

more volatile selenides may sometimes be separated and purified by distillation, but usually the products prove very difficult to separate. In addition, they tend to be unstable in light, and so considerable deposition of selenium tends to occur. Also, by nature of the original preparation, the solution is strongly alkaline, and this causes competing hydrolysis reactions to take place, further complicating the situation.

The situation is improved however, if an aqueous solution of sodium formaldehyde sulphoxylate, $NaSO_2CH_2OH$, is included in the preparation of the solution containing the selenide anions[131]. If the relative proportions of selenium, sodium formaldehyde sulphoxylate and hydroxide are manipulated, then the selenide dianion or diselenide dianion may be obtained as the main species. These dianions will then react with alkyl halides (57) to afford symmetrical selenides (128)[132] and diselenides (129)[132,133] respectively.

$$\underset{(57)}{RX} + Se^{2-} \longrightarrow \underset{(128)}{R_2Se}$$

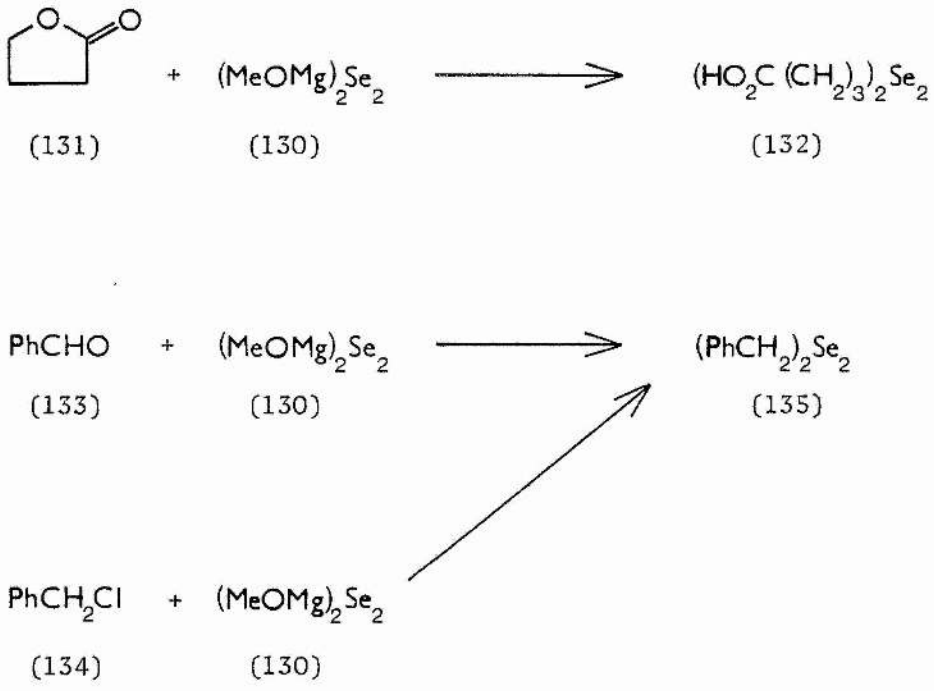
$$\underset{(57)}{RX} + Se_2^{2-} \longrightarrow \underset{(129)}{R_2Se_2}$$

These reactions have a wide use, but there is still the problem of contamination by the triselenide dianion and by polyselenide dianions, and the associated problems of separation and purification. This is unfortunate, since the reactions are otherwise quite simple, although care must be taken when handling sodium formaldehyde sulph-

oxylate since it is a very fine powder and can therefore cause dusting problems. In addition, exposure to air will cause the sodium formaldehyde sulphoxylate to decompose, releasing formaldehyde.

c) Bis(methoxymagnesium) Diselenide

Selenium reacts with magnesium and methanol to afford bis-(methoxymagnesium) diselenide (130), which may be obtained as a crystalline product[134]. When in solution in methanol, the compound affords highly reactive diselenide dianions which will effect nucleophilic displacement. Not only may alkyl halides be converted into diselenides, but the lactone (131) will afford the diselenide (132), and benzaldehyde (133) and benzyl chloride (134) afford dibenzyl diselenide (135).



The advantages of this reagent are that a non-aqueous solvent may be used, and so the competing hydrolytic side-reactions are absent.

Once again however, contamination by polyselenide anions may occur.

7) Selenium Halides And Oxyhalides

Once again, few compounds of this type have been used for inserting selenium into organic compounds; only selenium monochloride, tetrachloride, oxychloride and the bromine analogues have been investigated. The selenium halides are prepared by the reaction of the elements, although maintaining the desired stoichiometry is difficult, since exchange reactions occur quite readily[135-139].

$$Se_2X_2 \rightleftharpoons SeX_2 + Se$$

$$SeX_4 + Se \rightleftharpoons 2\ SeX_2$$

The oxyhalides are prepared from selenium dioxide and hydrogen halide (136) in the presence of concentrated sulphuric acid.

$$SeO_2 + 2\ HX \xrightarrow{\text{conc. } H_2SO_4} SeOX_2$$

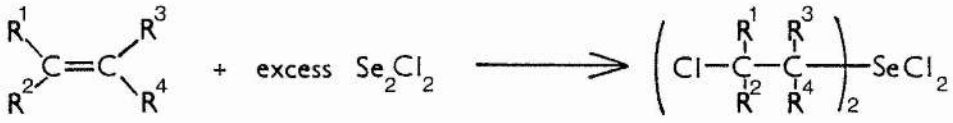
(136)

a) Addition To Multiple Bonds

The reaction of selenium monochloride with isolated double bonds has been widely studied[139-141]. Compounds (137) will react with selenium monochloride to give the selenides (138). The reaction conditions may vary quite considerably between reactions, depending

upon the reactivity of the olefin. However, it appears to be necessary not to have an excess of selenium monochloride, otherwise the corresponding selenide dichlorides (139) are formed.

(137) (138)

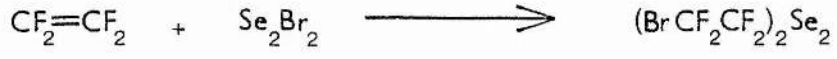


(137) (139)

If a compound containing two suitably positioned double bonds (140) is reacted in this manner, then a tetrahydroselenophene (141) is obtained[139].

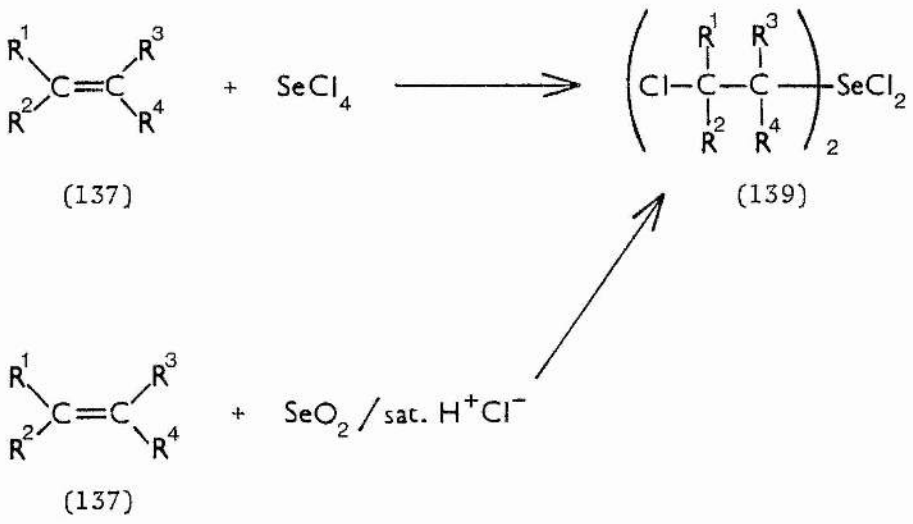
(140) (141)

Only one reaction employing selenium monobromide in a similar manner has been investigated[142]. Selenium monobromide reacts with tetrafluoroethene (142) to give the diselenide (143).



(142) (143)

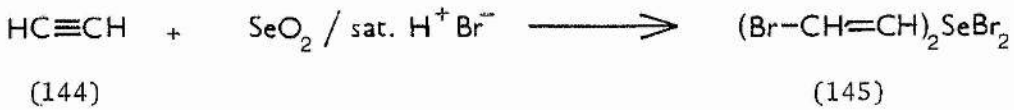
The selenide dichloride (139) may also be obtained by the reaction of olefin (137) with selenium tetrachloride[143], or with selenium dioxide in a saturated solution of aqueous hydrogen chloride[144].



(137) (139)

(137)

An analogous reaction occurs using selenium dioxide and a saturated aqueous solution of hydrogen bromide[144]. These conditions will convert acetylene (144) to the selenide dibromide (145)[144]. Acetylene (144) will also react with selenium tetrachloride to give the selenide dichloride (146)[143].



(144) (145)

(144) (146)

b) Electrophilic Substitution Reactions

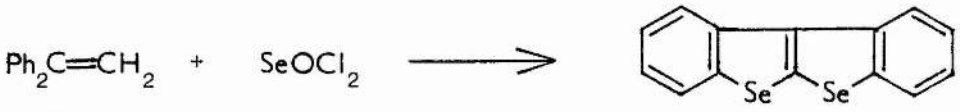
A variety of reactions are known to occur between suitably substituted organic compounds and either selenium tetrachloride or selenium oxychloride, although the mechanisms of these reactions are not always understood. Ketones (147) will react quite readily under mild conditions with either selenium tetrachloride[145,146] or with selenium oxychloride[147] to afford selenide dichlorides (148).

(147) (148)

Anilines (74) will react with both selenium monochloride and selenium oxychloride to give the selenide (149)[16].

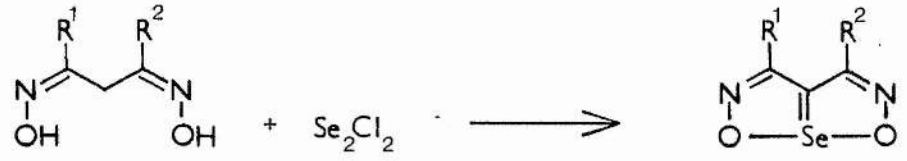
(74) (149)

Selenium oxychloride may also be used to obtain novel heterocyclic compounds. Thus, 1,1-diphenylethene (150) affords the compound (151)[148].

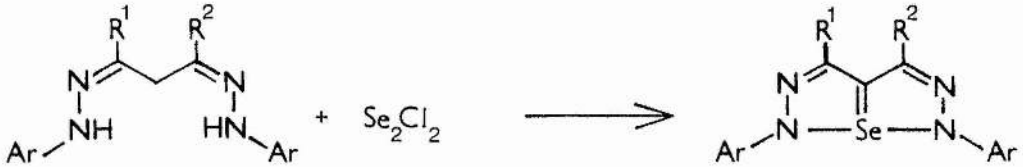


(150) (151)

Reactions with several other types of organic compounds have yielded apparently anomalous results, and further work is required. However, two examples of more recent work have seen selenium monochloride used in the preparation of 1,6-dioxa-6aλ^4-selena-2,5-diazapentalenes (109) and 6aλ^4-selena-1,2,5,6-tetraazapentalenes (110) from the corresponding dioximes (107)[113-116] and bis-hydrazones (108)[114,117].



(107) (109)



(108) (110)

Ar = C_6H_5, 2,4-$(NO_2)_2$-C_6H_3

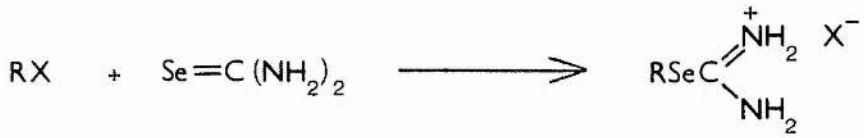
Thus, the reagents offer a comparatively mild and easy means of inserting selenium into organic compounds, but purity and handling problems are obvious disadvantages.

B. Simple Organic Reagents

Only a few organic derivatives are known to have general applicability for the formation of new carbon-selenium bonds.

1) Selenourea

Selenourea (35) is readily alkylated to give isoselenouronium salts (152) from alkyl halides (57) under very mild conditions in organic solvents[149], thereby avoiding competing hydrolytic side-reactions.



(57) (35) (152)

In most cases, the isoselenouronium salt (152) may be isolated and then hydrolysed under basic conditions to the corresponding selenol. This may in turn undergo further reaction if desired.

Hence, selenourea is a comparatively advantageous reagent for the insertion of selenium into organic compounds.

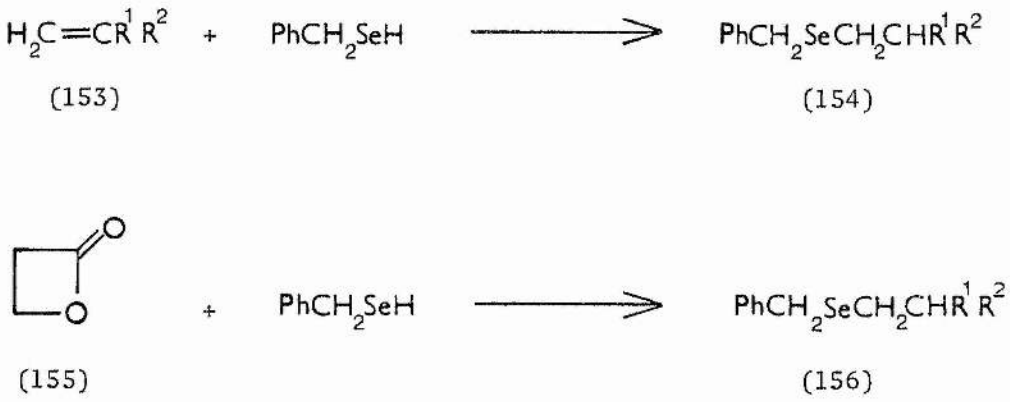
2) Benzylselenol

In the synthesis of complex aliphatic selenols, it is frequently necessary to introduce the selenium substituent prior to subsequent steps. The relatively sensitive selenium substituent must therefore be protected, and the protection be removed at a later stage. Unfortunately, most means of protection have considerable drawbacks and

limitations. The benzylselenium moiety has the advantage however, that it is stable to a wide variety of reagents and reaction conditions, and may be removed very efficiently by reduction with sodium in liquid ammonia[150].

Benzylselenol can be prepared by the reaction of benzylmagnesium bromide with selenium[150], or more cleanly, by the reduction of dibenzyldiselenide with lithium aluminium hydride[16]. Dibenzyldiselenide can be prepared as previously discussed in Section 1.A.6).

Benzylselenol reacts as might be expected of a selenium nucleophile, except that the resulting selenides are relatively stable and can be easily isolated. It will undergo addition to double bonds[151,152], as for the conversion of olefin (153) to selenide (154), and will ring-open lactones[153-155], such as propiolactone (155) to give the selenide (156).



(153) (154)

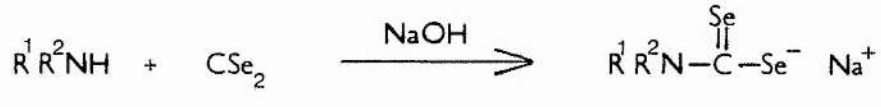
(155) (156)

More recent work involving the selective displacement of protecting groups during the synthesis of peptides[156,157], suggests that benzylselenol will find increasing use in years to come.

3) Carbon Diselenide

Carbon diselenide may be prepared from carbon tetrachloride[158], or more efficiently, from the reaction of dichloromethane with molten selenium[159,160]. The dense liquid is extremely nauseating, and requires very careful handling and the use of chemical traps, such as charcoal in ethanolic hydroxide solution.

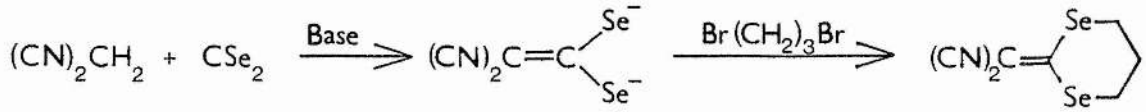
Reactions involving carbon diselenide do not always involve the formation of new carbon-selenium bonds, but may still be justifiably included here, since selenium is inserted into the organic molecules. Reactions with primary amines afford symmetrical selenoureas, whilst those with secondary amines (157) afford N,N-dialkyldiselenocarbamate salts (158)[160].



(157) (158)

It is very important to avoid an excess of carbon diselenide, or polymerisation is likely to occur.

Carbon diselenide will also react quite readily with activated methylene groups[161], such as that in dicyanomethane (159) which affords the corresponding 1,1-diselenolate anion (160), and which may be trapped by the reaction with 1,3-dibromopropane to yield the 1,3-diselenan (161).



(159) (160) (161)

Carbon diselenide has been observed to react with carbon tetrachloride to afford the compound (162)[162], and more recently, with selenium monobromide to give compound (163)[163].

(162)

(163)

Unfortunately, the properties of carbon diselenide, and the problems associated with handling it, make this reagent a less popular choice for the insertion of selenium into organic molecules.

2. The Introduction Of Sulphur Into Carbonyl Compounds Using Organothiophosphorus Reagents

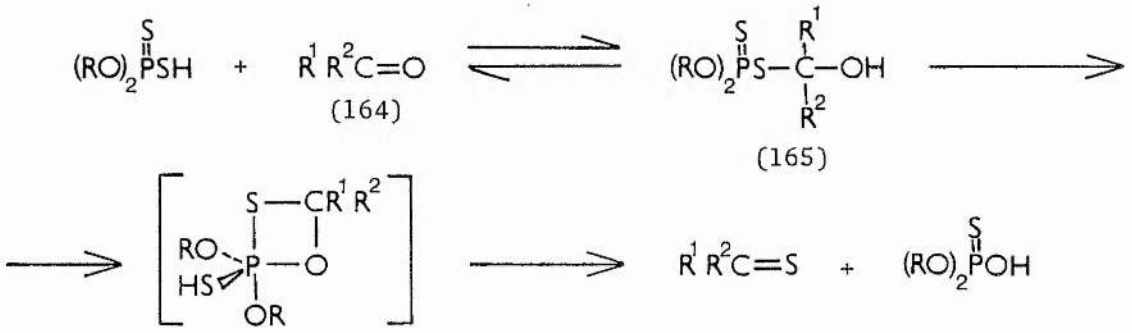
It has previously been shown in Section 1.A.1)b) that phosphine selenides may be obtained from trivalent phosphines. Since it is this class of compound that was primarily employed as the selenium-transfer reagent in the work embodied in this thesis, it is appropriate to consider on a comparative basis, the work that has been carried out using organothiophosphorus compounds to insert sulphur into organic compounds. The discussion will be limited to reactions involving carbonyl functions, primarily aldehydic and ketonic functions, and also those reactions involving phosphine sulphides.

A recent review by Cherkasov, Kutyrev and Pudovik has dealt with organothiophosphorus reagents quite comprehensively[164]. There are two main types of reagent to be considered.

A. Phosphorus Thioacids And Their Derivatives

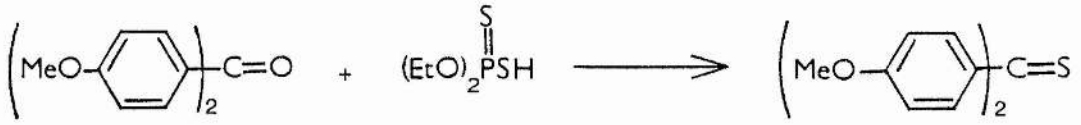
1) Phosphorus Dithioacids

Since phosphorus dithioacids not only have an acid function with a pK_a of between two and four, but have considerable nucleophilic properties as well, they are easily attached to the carbonyl function of aldehydes and ketones (164), usually in a reversible reaction. The resulting dithiophosphates (165) may be converted into the corresponding thiocarbonyl compounds (166) and phosphorus thioacids (167), via the cyclic intermediate (168)[165].

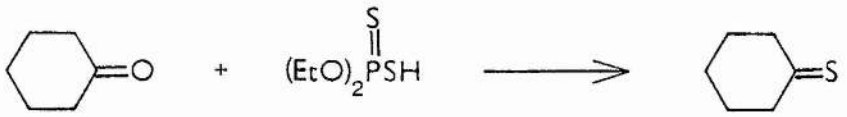


(164) (165) (168) (166) (167)

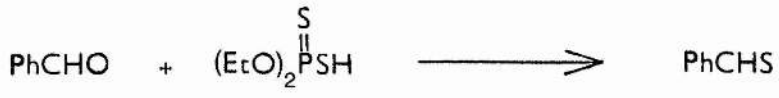
If the compounds (169), (170) and (133) are treated with O,O'-diethyldithiophosphoric acid at moderate temperatures for between one and two days, then the thiocarbonyl analogues (171), (172) and (173) respectively, are obtained in good to excellent yields.



(169) (171)

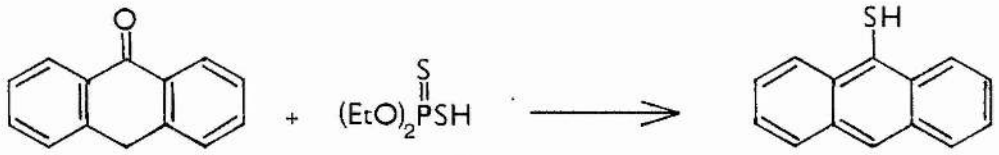


(170) (172)



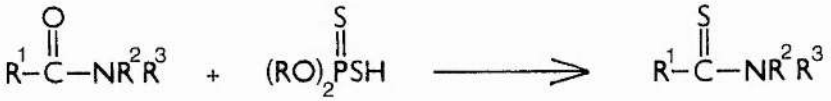
(133) (173)

However, if the product can achieve delocalisation, then this may affect the result of the reaction, as in the case of the conversion of anthrone (174) to the anthracene thiol (175).



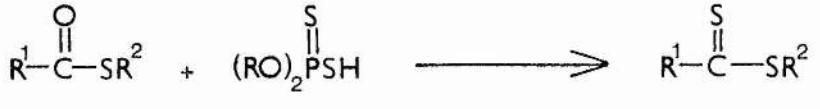
(174) (175)

Phosphorus dithioacids will also react with carboxamides (87) to afford thiocarboxamides (176)[166], with carboxylates (177) to afford a mixture of esters (178) and (179)[167], with thiocarboxylates (180) to give the dithiocarboxylic esters (179)[167], and with isocyanates (181) to afford isothiocyanates (182)[168].

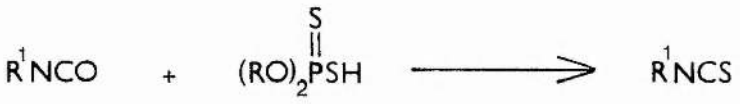


(87) (176)

(177) (178) (179)



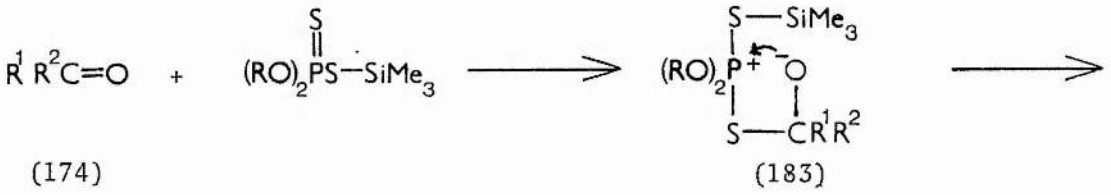
(180) (179)



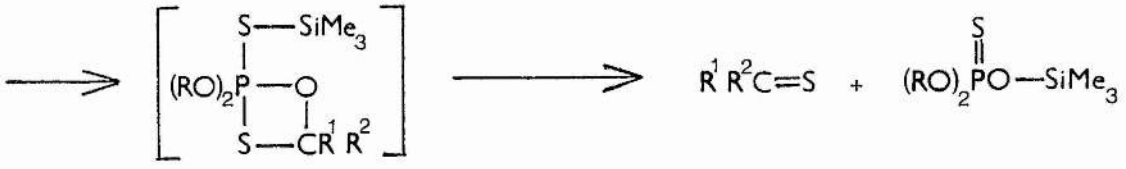
(181) (182)

2) S-Trimethylsilyl Esters Of Phosphorus Dithioacids

These esters are also effective thionating reagents, since the silicon atom has a strong oxygenphilicity due to the fact that silicon-oxygen bonds are considerably stronger than silicon-sulphur bonds[169]. The result is that S-trimethylsilyldithiophosphates undergo reaction with aldehydic and ketonic carbonyl groups (164) to form the intermediates (183), which are easily converted into the analogous thiocarbonyl compounds (166) and O-trimethylsilylthiophosphates (184) via the cyclic intermediates (185).

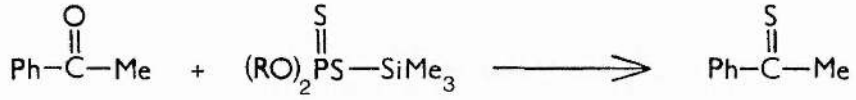


(174) (183)



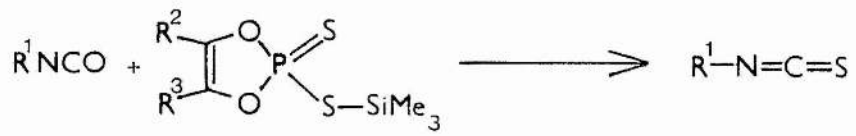
(185) (166) (184)

This type of reaction is especially favourable for the preparation of aromatic thiocarbonyl compounds. The preparation of thioacetophenone (186) from acetophenone (187) is quantitative[170].



(187) (186)

It is somewhat more difficult to obtain isothiocyanates (182) from isocyanates (181) using S-trimethylsilyldithiophosphates. The most efficient method discovered so far involves the introduction of a 1,2-dioxyalkene or 1,2-dioxyarylene substituent on to the phosphorus atom[164], as in compound (188). This affords several isothiocyanates (182) in excellent yields under mild conditions.



(181) (188) (182)

It is hoped that reagents of this type will prove to be as effective upon aldehydes and ketones.

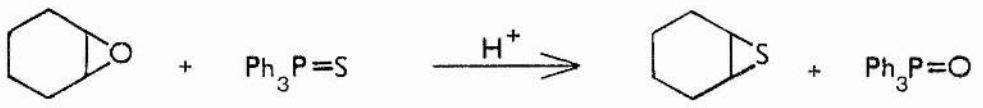
3) Thiophosphates And Thiophosphoric Diamides

These compounds have not been observed to react with aldehydes or ketones, but only with amides, to give, amongst other products, analogous thioamides[166,171]. The nature of the amide used is very import-

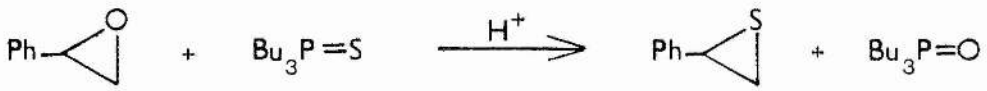
ant in deciding the course of the reaction.

4) Phosphine Sulphides

Phosphine sulphides have not been observed to undergo reactions with either aldehydes or ketones, but trialkyl- and triarylphosphine sulphides do react with oxiranes in the presence of trifluoroacetic acid under mild conditions to give thiiranes in moderate yields[172]. Cyclohexene oxide (189) reacts with triphenylphosphine sulphide to give cyclohexene sulphide (190), and styrene oxide (191) reacts with tri-n-butylphosphine sulphide to afford the corresponding thiirane (192).



(189) (190)

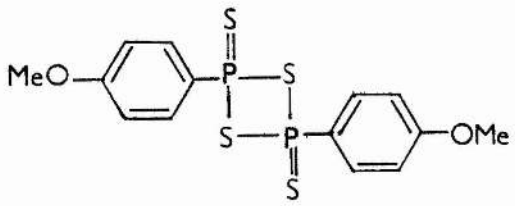


(191) (192)

These reagents are therefore very important, as they provide an efficient means of obtaining sulphur compounds under mild conditions as a result of their pronounced nucleophilicity and the lower strength of the phosphorus-sulphur bond when compared with phosphorus-oxygen bonds.

B. Lawesson's Reagent

2,4-Bis(4-methoxyphenyl)-1,2,3,4-dithiadiphosphetane-2,4-disulphide (193), more commonly known as Lawesson's Reagent, is one of the most effective thionating reagents presently known. It may be prepared directly from anisole, phosphorus and sulphur[173].



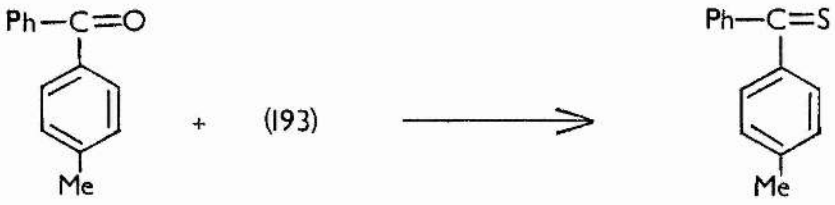
(193)

1) Reactions With Ketones

Lawesson's Reagent reacts with ketones to afford the corresponding thioketones in high yield when the reactions are carried out in anhydrous toluene at 110°C under nitrogen[174]. Benzophenone (194) affords thiobenzophenone (195), 4-methylbenzophenone (196) yields the 4-methylthiobenzophenone (197), 3-nitrobenzophenone (198) gives 3-nitrothiobenzophenone (199), and the dicyclopropyl ketone (200) produces the thioketone (201).

$Ph_2C{=}O$ + (193) ⟶ $Ph_2C{=}S$

(194) (195)

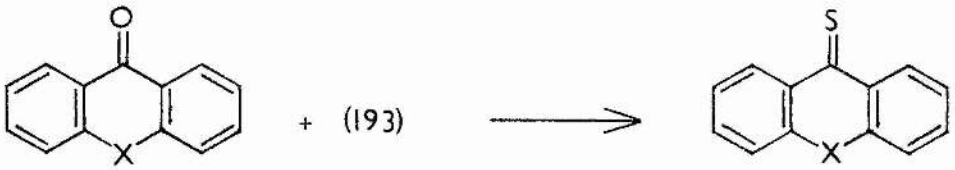


(196) (197)

(198) (199)

(200) (201)

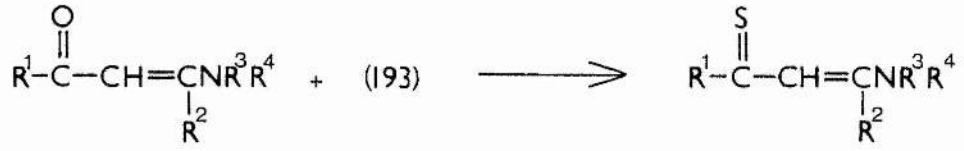
Cyclic ketones may also be thionated, although it has been noted that the speed of reaction is solvent dependent[175]. However, compounds (202) may be converted to the sulphur analogues (203)[175-177].



(202) (203)

X = O, S, N-H

If α,β-unsaturated ketones are reacted with Lawesson's Reagent, the corresponding thioketones are formed, and can be isolated if they are sufficiently stable[176]. Enamines (204) afford enaminothiones (205)[177,178], cyclic ketones (206) give cyclic thioketones (207)[176], whilst cyclic enaminones (208) form the corresponding enaminothiones (209)[177].



(204) (205)

(206) (207)

(208) (209)

In certain cases however, such as with sterically hindered ketones, thionation does not occur.

2) Reactions With Esters Of (Thio)Carboxylic Acids

The reaction of Lawesson's Reagent with the esters of carboxylic acids (177) and thiocarboxylic acids (180) is usually straight forward, producing thioacylates (178) and dithiocarboxylates (179) respectively, and in good yield[179].

(177) (178)

(180) (179)

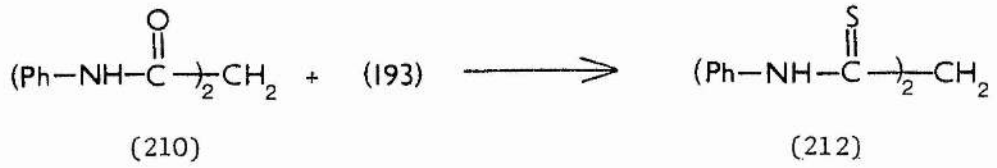
3) Reactions With Amides Of Carboxylic Acids

Carboxamides (87) react readily with Lawesson's Reagent to produce thiocarboxamides (176) in almost quantitative yield[180]. Varying the substituents R^2 and R^3 does not affect the course of the reaction, even when the reactive functions such as nitro, halo, and amino substituents are introduced.

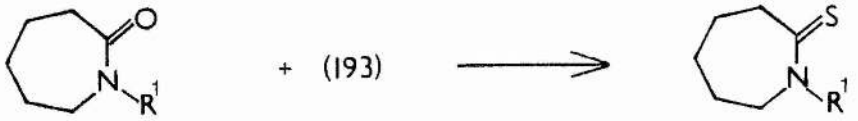
(87) (176)

Even bifunctional amides (210) and cyclic carboxamides (211)

react with Lawesson's Reagent to give the expected bisthioamides (212)[180] and cyclic thioamides (213)[164] respectively.

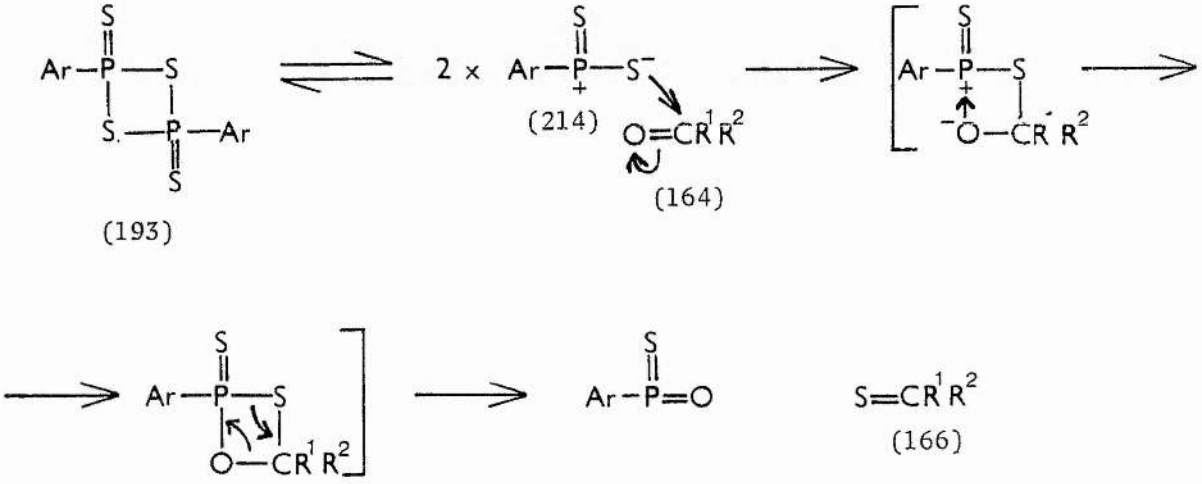


(210) (212)



(211) (213)

The mechanism of the reaction of Lawesson's Reagent (193) with carbonyl compounds (164) has only recently been considered. A recent review[181] proposes that the mechanism may be such that Lawesson's Reagent dissociates to produce the highly reactive dithiophosphine ylide (214). This would then react with the carbonyl compound (164) in a manner analogous to the Wittig reaction to produce the thiocarbonyl product (166) via a four-centre cyclic intermediate.



(193) (214) (164) (166)

Ar = 4-OMe-C_6H_4

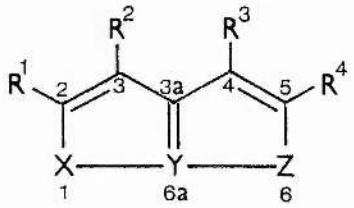
An analogous type of mechanism may be proposed for the reaction of all $\geqslant P=S$ reagents with carbonyl compounds. The analogy may even be extended to $\geqslant P=Se$ reagents.

In conclusion, not only is Lawesson's Reagent one of the most effective reagents to carry out the thionation of organic compounds, but its advantages of being easily prepared and simple to use, and of being able to produce high yields of readily isolatable products, make it probably the most convenient. Further studies employing this reagent and its substituted analogues will undoubtably be carried out in the future.

3. 1,6,6aλ^4-Triheterapentalenes Containing Selenium

Since the reactions of (1,2-dithiol-3-ylidene)carbaldehydes and phenylphosphonoselenoic dichloride to give 1,6aλ^4-dithia-6-selena-pentalenes were carried out during the work embodied in this thesis, it is appropriate that there should be a discussion about the 1,6,6aλ^4-triheterapentalenes that contain selenium.

1,6,6aλ^4-Triheterapentalenes may be depicted by the general structural formula (215), where X and Z may be O,S,Se or N-R, and where Y may be S,Se or Te. Structurally similar analogues are also known where one or more carbon atoms are replaced by nitrogen atoms.



(215)

Reviews of the chemistry and properties of these compounds have been written by various authors[182-191]. For the purposes of this discussion, however, only the literature pertaining to the particular classes of triheterapentalenes containing selenium will be considered. Section headings will refer to the general structure (215).

A. Structural Studies

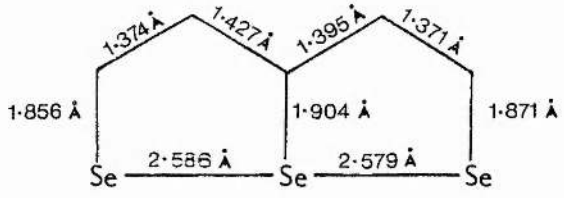
1,6,6aλ^4-Triheterapentalenes and related systems have been extensively studied using various techniques to assist structural analyses. In particular, X-ray crystallography and n.m.r. spectroscopy have played very important roles in the assignment of structures to these compounds.

1) X-Ray Crystallography

a) 1,6,6aλ^4-Triselenapentalenes (215 : X,Y,Z = Se)

Crystal structure data of 1,6,6aλ^4-triselenapentalene (216)[192] indicates that the molecule is planar, with the selenium atoms adopting an almost collinear arrangement.

However, the molecule does not exhibit C_{2v} symmetry, and this is attributed to the relatively short intermolecular distances between molecules in the same crystallographic unit, resulting in a degree of intermolecular attraction, and hence distortion of the molecule.



(216)

The Se-Se bond lengths (2.586 Å and 2.579 Å) are approximately 10% greater than the length of the corresponding two-electron, covalent single bond (2.34 Å)[193], but considerably shorter than the

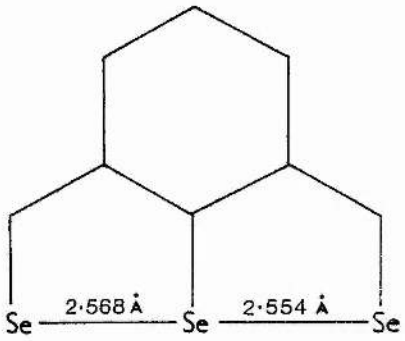
sum of the appropriate Van der Waal's radii (4.00 Å)[193]. This would suggest that, although the bond order of the Se-Se bonds is less than unity, significant bonding interactions occur between the two lateral selenium atoms and the central selenium atom.

The lateral C-Se bond lengths (1.856 Å and 1.871 Å) are less than that of the corresponding covalent single bond (1.94 Å)[193], but greater than that of the carbon-selenium double bond (1.74 Å)[193]. Similarly, the central C-Se bond also exhibits a bond length (1.904 Å) which is intermediate in value between these two extremes. This indicates that all the C-Se bonds exhibit bond orders of between one and two.

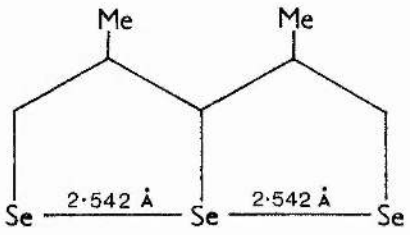
This is also the case for the C-C bonds. The lateral C-C bonds (1.374 Å and 1.371 Å) are certainly shorter in length than the central C-C bonds (1.427 Å and 1.395 Å), but they are all intermediate in value between the lengths of a covalent carbon-carbon single bond (1.54 Å)[193] and a corresponding double bond (1.34 Å)[193]. Indeed, the bond lengths exhibited are comparable to those observed in naphthalene[194], indicating that the aromaticity of the superimposed π-electron system is similar to that of the 10 π-electron system of naphthalene.

The unusual bonding exhibited in the collinear selenium sequence is therefore both σ and π in character, but the bonds are weaker than the other bonds in the molecule. They are therefore more liable to changes in bond length when either the σ-system or the π-system is perturbed. Such perturbations may be caused by alterations in the intramolecular or intermolecular environments of the molecule. As previously explained, the presence of just such an intermolecular perturbation is responsible for the absence of C_{2v} symmetry on this occasion.

Other members of this class of triheterapentalene that have been examined crystallographically are compounds (217)[195] and (218)[196].



(217)



(218)

Only preliminary details of compound (218) have been published, and so it is uncertain whether the Se-Se bond length shown (2.542 Å) is representative or merely an average of two quite different Se-Se bond lengths. Nevertheless, the data indicates that the triheterapentalene skeleton is planar.

For compound (217), the presence of relatively short intermolecular distances has resulted in the loss of C_{2v} symmetry, but the triheterapentalene skeleton is still planar.

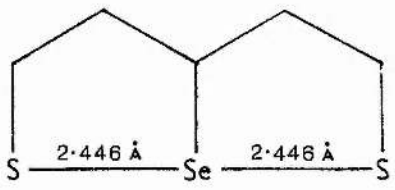
The Se-Se bond lengths (2.568 Å and 2.554 Å) are approximately 10% and 9% greater than the length of the corresponding two-electron, covalent single bond (2.34 Å)[193], and so are considerably shorter than the sum of the Van der Waal's radii of two selenium atoms (4.00 Å)[193]. The Se-Se bond order is once more less than unity, as was the case for compound (216).

Although conclusions are difficult to substantiate when so few members of this class of triheterapentalenes have been examined crystallographically, the fact that the Se-Se bonds are between 9% and

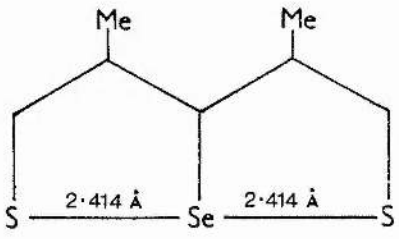
10% greater in length than the covalent selenium-selenium single bond suggests that for these compounds at least, a bicyclic structure with bonding interaction between the selenium atoms seems likely. By analogy with 1,6,6aλ^4-trithiapentalenes, this may be accounted for by the Gleiter-Hoffmann theory of three-centre, four-electron bonding[197].

b) <u>1,6-Dithia-6aλ^4-selenapentalenes</u> (215 : X,Z = S ; Y = Se)

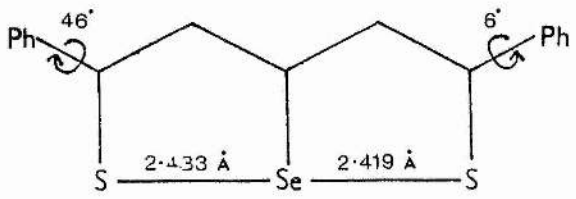
Structural analyses of compounds (219)[198], (220)[199] and (221)[200] have been undertaken, and indicate that the triheterapentalene skeleton of all three compounds is apparently planar, that the sulphur-selenium sequence is approximately collinear, and that compounds (219) and (220) exhibit C_{2v} symmetry. Although compound (221) is symmetrically substituted, the fact that it does not possess C_{2v} symmetry in the solid state may be accounted for by the different angles of twist of the two phenyl substituents out of the plane of the triheterapentalene skeleton, thereby causing intramolecular perturbation of the S-Se bond lengths.



(219)



(220)



(221)

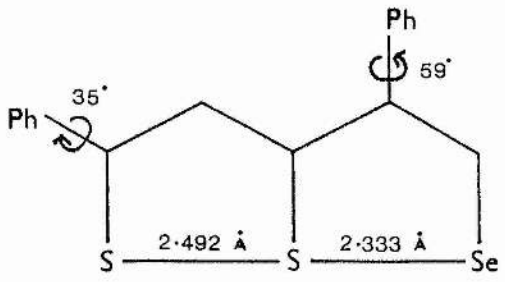
The S-Se bond lengths of compound (219) (2.446 Å) are approximately 11% greater than the length of the corresponding two-electron, covalent single bond (2.21 Å)[193], but considerably shorter than the sum of the appropriate Van der Waal's radii (3.85 Å)[193]. Once again, it appears that a bond order of less than unity is present, with significant bonding interactions occurring between the two lateral sulphur atoms and the central selenium atom. This is confirmed by compounds (220) and (221), whose S-Se bond lengths are between 9% and 10% greater in length than the sulphur-selenium covalent single bond length (2.21 Å)[193].

It may be observed that not only are the twist angles of the phenyl substituents in compound (221) different, but that the substituent of the ring with the longer S-Se bond (2.433 Å) has the greater twist angle (46°). This is analogous to the situation observed for the corresponding trithiapentalene[201], and is in accord with the proposals made on the basis of CNDO/2 calculations[202].

When these compounds are compared with 1,6,6aλ^4-triselenapentalenes, it may be concluded that the same type of bonding is present for both. Therefore, it is likely that 1,6-dithia-6aλ^4-selenapentalenes possess a bicyclic structure, with considerable bonding interaction occurring between the lateral sulphur atoms and the central selenium atom.

c) <u>1,6aλ^4-Dithia-6-selenapentalenes</u> (215 : X,Y = S ; Z = Se)

Only one member, compound (56), of this type of triheterapentalene has been examined crystallographically[98], and the triheterapentalene skeleton was found to be planar.



(56)

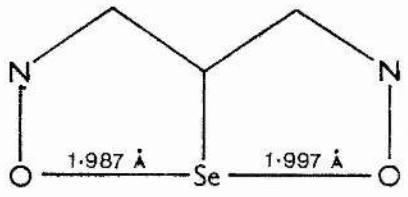
The S-S bond length in compound (56) (2.492 Å) is 19% greater than the length of the corresponding two-electron, covalent single bond (2.10 Å)[203], whilst the S-Se bond length (2.333 Å) is only 6% greater than the length of a covalent sulphur-selenium single bond (2.21 Å)[193]. These values seem rather extreme with respect to each other until they are compared with the values obtained from the corresponding trithiapentalene[204], namely 19% and 6% respectively. The data is obviously in good agreement, and the large difference in values within each compound may be accounted for by the intramolecular perturbations caused by the phenyl substituents. The perturbations are consistent with the proposals resulting from CNDO/2 calculations[202]; namely, that a 2-phenyl substituent with a relatively large angle of twist will lengthen the adjacent S-S bond, whilst a 3-phenyl substituent will shorten it. When applied to compound (56), this would entail a long S-S bond and a short S-Se bond, as observed.

Compound (56), as the sole representative of 1,6aλ^4-dithia-6-selenapentalenes that has been examined crystallographically, may therefore be considered to be bicyclic, and possessing considerable bonding interaction between the lateral sulphur and selenium atoms, and the central sulphur atom.

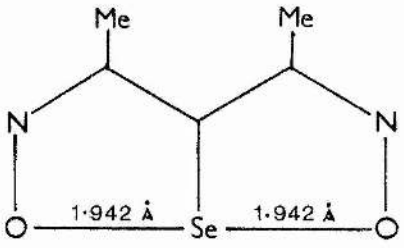
d) 1,6-Dioxa-6aλ^4-selena-2,5-diazapentalenes

(215 : X,Z = O ; Y = Se ; C_2,C_5 = N)

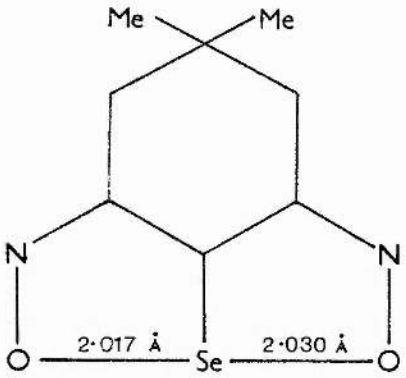
Crystallographic data for compounds (222)[196], (223)[196], and (224)[205] indicate that the triheterapentalene skeletons are planar, but that the oxygen and selenium atoms may no longer be considered to be collinear, since the selenium atoms are 'extended out' of the collinearity, so that the O-Se-O bond angles are between 160° and 168°.



(222)



(223)



(224)

The O-Se bond lengths of compound (222) (1.987 Å and 1.997 Å) are approximately 4% and 5% greater in length respectively, than the corresponding two-electron, covalent single bond length (1.91 Å)[193],

but considerably shorter than the sum of the Van der Waal's radii (3.40 Å)[193]. The O-Se bond lengths of compound (224) (2.017 Å and 2.030 Å) are 6% greater than the length of 1.91 Å, whilst the average O-Se bond length of compound (223) (1.942 Å) is 2% greater. Full details for compound (223) have not been published however.

This suggests that although the bond orders are less than unity, significant interactions occur between the lateral oxygen atoms and the central selenium atoms.

The observed lengths of the N-O, C-N, C-C_{3a}, and C-Se bonds are all intermediate in value between the lengths of the corresponding covalent single and double bonds[193], and so they exhibit bond orders of between one and two. Finally, the virtual equality of the O-Se bond lengths of each compound must be the result of intramolecular bonding, rather than of crystal packing, since there are no significantly short intermolecular distances.

Hence, since these compounds apparently possess the same type of bonding as other selenium-containing triheterapentalene compounds examined, they may be considered to be bicyclic, with considerable bonding interactions between the lateral oxygen atoms and the central selenium atoms.

2) Nuclear Magnetic Resonance Spectroscopy

^{1}H N.m.r. spectra of all symmetrically substituted, selenium-containing triheterapentalenes[68,113-115,117,126,206] show that there is equivalence of the ring protons and of symmetrical substituents, indicating that these compounds have real or time-averaged C_{2v} symmetry in solution.

Therefore, on the basis of ^{1}H n.m.r. spectroscopic evidence, either all these molecules have C_{2v} symmetry, or the equivalence is due to two rapidly interconverting valence tautomers (225) and (226), resulting in time-averaged C_{2v} symmetry in solution.

(225) (226)

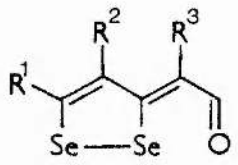
Variable temperature ^{1}H n.m.r. studies[113] have shown no departure from magnetic equivalence between 40°C and -60°C. However, this is not conclusive evidence, since interconversion of the two tautomers (225) and (226) may still be too rapid, even at -60°C.

Further evidence may be provided from a comparison of the ^{1}H n.m.r. data of appropriate selenium-containing triheterapentalenes and of stable carboselenaldehydes in an attempt to decide whether the triheterapentalenes exist as the bicyclic structure depicted by (227), or the monocyclic structure represented by (228).

(227) (228)

The chemical shift values of the carboselenaldehyde protons in stable indolizine and pyrrolo[2,1-b]thiazole 1- and 3-carboselenaldehydes may be used to obtain a range within which the chemical shift values of a stable carboselenaldehyde proton might normally be expected to occur. The appropriate chemical shift values of these

compounds normally occur in the range δ 11.94 to 13.00 ppm[74], and even when highly polarised in the sense $R^{+}=CH-Se^{-}$, are unlikely to occur much further upfield.



(125)

However, with the exception of the anomalous (1,2-diselenol-3-ylidene)aldehydes (125), whose corresponding chemical shift values normally occur in the range δ 8.33 to 8.92 ppm[68], the appropriate shift values of all relevant selenium-containing triheterapentalenes normally occur in the range δ 9.69 to 11.08 ppm[68,75,128,206-208]. This would suggest that these compounds do not contain the environment (228), but rather the environment (227). This evidence is not conclusive however, since the observed chemical shift values may be the average obtained from the two environments rapidly interconverting.

^{13}C N.m.r. spectroscopy has been employed, albeit sparingly, and has been carried out on various 1,6-dioxa-6aλ^{4}-selena-2,5-diazapentalenes and 6aλ^{4}-selena-1,2,5,6-tetraazapentalenes[115,117]. It reinforces the evidence obtained by ^{1}H n.m.r. spectroscopy; namely that these symmetrically substituted selenium-containing triheterapentalenes exhibit equivalence of substituent protons, and therefore possess real or time-averaged C_{2v} symmetry in solution.

Therefore, if all the available n.m.r. data is considered in conjunction with the crystallographic data, it would suggest that

these compounds do possess C_{2v} symmetry within the temperature range studied.

3) Miscellaneous Spectroscopic Techniques

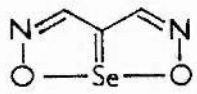
Several other spectroscopic techniques have been applied to selenium-containing 1,6,6aλ^4-triheterapentalenes, but have yielded relatively little structural information.

Mass spectroscopy has been applied to several such compounds[117,206,209,210], and the fragmentation patterns have been observed to be similar to those of corresponding sulphur analogues. One difference however, is the more facile loss of selenium compared with sulphur, since certain peaks, such as $[M-X_3H]^+$, that are common for selenium-containing triheterapentalenes are usually less intense, or even absent, for the sulphur analogues. Nevertheless, the considerable similarity in the fragmentation patterns of corresponding triheterapentalenes suggests that the bonding in selenium and sulphur analogues may be comparable, although this is far from conclusive evidence.

Strong similarities in the infra-red and ultra-violet/visible spectra provide further evidence that the bonding in selenium-containing triheterapentalenes is analogous to that in corresponding sulphur compounds. One feature to note from the infra-red spectra, is that (1,2-diselenol-3-ylidene)aldehydes (125) possess an absorption of medium intensity between 1530 cm^{-1} and 1575 cm^{-1} [68], as do corresponding sulphur analogues[211,212], indicating that there must be some interaction between the oxygen atoms and the central selenium atoms, since α,β-unsaturated aldehydes and ketones normally exhibit the

corresponding absorption between 1660 cm^{-1} and 1705 cm^{-1}. Otherwise, the only slight differences to be observed are that some absorptions in the visible region for selenium-containing triheterapentalenes experience a slight shift to longer wavelengths relative to their sulphur analogues[68].

A gas-phase photo-electron spectrum of compound (222) has been obtained[213], and used as evidence for C_{2v} symmetry in this compound. However, previous use of this technique on trithiapentalenes has sometimes given inconclusive results[214-216].



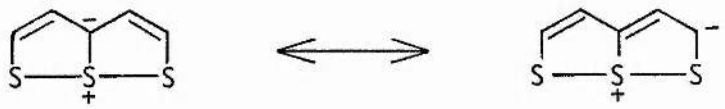
(222)

In conclusion therefore, these techniques, although occasionally yielding some structural information, are not of primary importance in the elucidation of the structure and bonding of selenium-containing 1,6,6aλ^4-triheterapentalenes.

B. Bonding

The type of bonding present in 1,6,6aλ^4-triheterapentalenes has been discussed frequently, as various authors attempt to account for the observed planarity, heteroatom collinearity, and C_{2v} symmetry. Various theories have been proposed to describe the bonding in these compounds, but since the earliest known and most extensively studied compounds of this type have been the trithiapentalenes, the majority of this work relates to them. However, it has previously been described how similar the bonding must be between selenium-containing triheterapentalenes and their sulphur analogues, so that the conclusions drawn for trithiapentalenes may equally well apply to their selenium isosteres.

One of the earliest structures proposed for 1,6,6aλ^4-trithiapentalenes was (229)[217]. However, this structure would give rise to the structure (230), thereby implying that electrophilic attack should occur at C_2, and this is inconsistent with experimental observations[218-225].



(229) (230)

Another hypothesis was that of 'single bond - no bond' valence tautomers, as shown by structures (231) and (232)[226-228].

(231) (232)

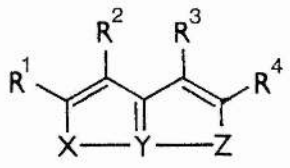
Shortly after the hypothesis of 'single bond - no bond' valence tautomers was presented, it was proposed that the central heteroatom underwent valence-shell expansion in order to enable its d-orbitals to participate in the σ-bonding[229-232]. Indeed, when d-orbitals were assumed to participate, CNDO/2[202] and Extended Huckel calculations[197] appeared to give the best correlation with crystal structure data. However, more recent ab initio and CNDO calculations have questioned whether in fact the d-orbitals do participate in the σ-bonding[215,233-235].

The presently accepted theory for the bonding in 1,6,6aλ^4-triheterapentalenes describes the three heteroatoms as being held together by a four-electron, three-centre σ-bond, with superimposed π-bonding over the two rings[197]. Three atomic p-orbitals, comprising one from each heteroatom, form three molecular orbitals; one antibonding, one non-bonding, and one bonding. Four electrons, one from each lateral heteroatom and two from the central one, fully occupy the non-bonding and bonding orbitals. The electron density of the bonding orbital is distributed over all three heteroatoms, which to a first approximation may then be considered as being held together by only one bonding orbital. This unusual bonding may then account for the relatively long heteroatom bond lengths in these compounds, and would require virtual collinearity of the three heteroatoms, as is indeed observed.

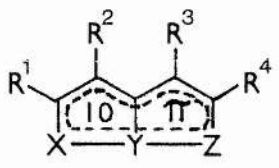
This bonding concept has also been proposed to account for the transition state in an S_N2 reaction[236], and for certain inorganic anions[237-244]. Indeed, the observed bond lengths in the linear triiodide anion are approximately 9% longer than the iodine-iodine bond length found for molecular iodine[237,240,241]. This percentage increase is comparable with that previously observed for 1,6,6aλ^4-triheterapentalenes.

In addition, it is proposed that each carbon atom and the central heteroatom contribute one p-electron, whilst the lateral heteroatoms each contribute two p-electrons to a superimposed 10 π-electron delocalised system, thereby inducing planarity, and also the apparent C_{2v} symmetry of symmetrically substituted 1,6,6aλ^4-triheterapentalenes. However, the resulting stabilisation, although beneficial, is not thought to be great, since the calculated $p_\pi - p_\pi$ overlap is small.

In general therefore, 1,6,6aλ^4-triheterapentalenes may be considered to be bicyclic, conveniently represented by either the structure (215) or (233).



(215)

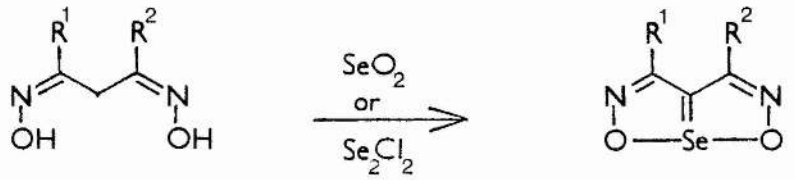


(233)

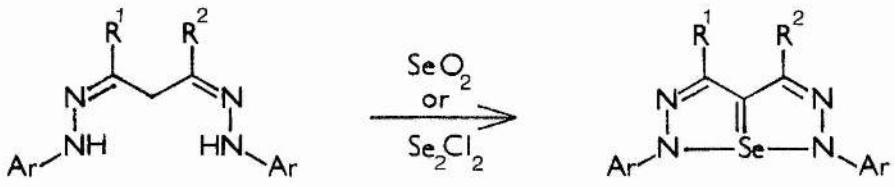
C. Synthesis Of Selenium-Containing 1,6,6aλ^4-Triheterapentalenes And Related Systems

1) From Dioximes And Bis-hydrazones

Selenium-containing 1,6,6aλ^4-triheterapentalenes may be synthesised directly from dioximes (107)[113-117] and from bis-hydrazones (108)[114,117], by reaction with either selenium dioxide or selenium monochloride. The yields of the resulting 1,6-dioxa-6aλ^4-selena-2,5-diazapentalenes (109) and 6aλ^4-selena-1,2,5,6-tetraazapentalenes (110) are very variable however, and the reaction times are often quite lengthy, but the reaction does appear to be quite general, within the limitations imposed by the need for the aryl substituent to be either a phenyl or a 2,4-dinitrophenyl group.



(107) (109)

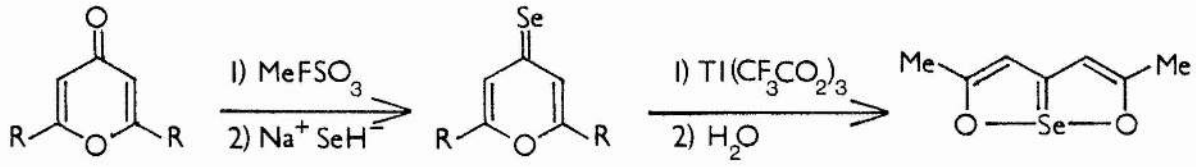


(108) (110)

Ar = C_6H_5 , $2,4-(NO_2)_2-C_6H_3$

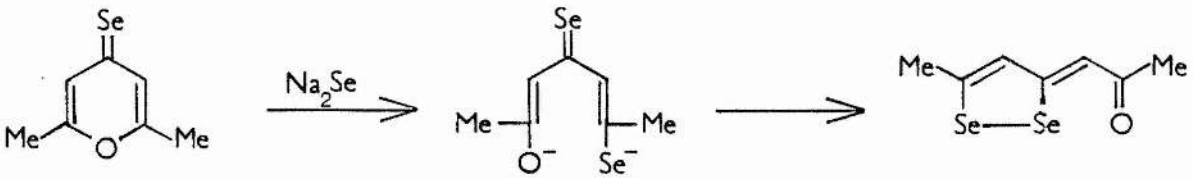
2) From 4H-(Thio)Pyran-4-selones

Since 4H-pyran-4-selones (44) are relatively unstable and lose selenium to form 4,4'-bipyranylidene derivatives, they are prepared from γ-pyrone (234) when required[73]. When reacted with thallium(III) trifluoroacetate, and then with water, under mild conditions, they afford 1,6-dioxa-6a λ^4-selenapentalenes (235)[73], although often in relatively poor yields.



(234) (44) (235)

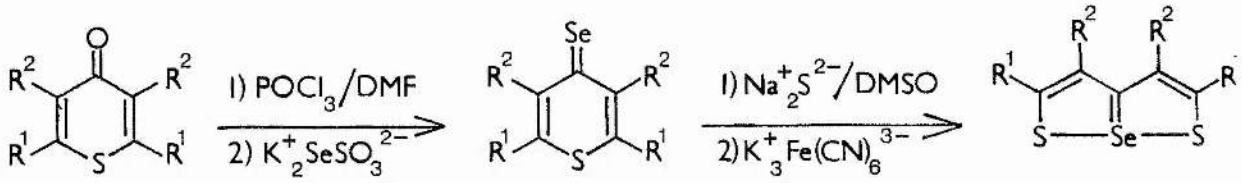
It has been reported that when the 2,6-dimethyl derivative (236) is treated with sodium selenide, the ketone (237) is obtained[245], presumably via the intermediate (238).



(236) (238) (237)

4H-Thiopyran-4-selones (124), themselves prepared from 4H-thiopyran-4-ones (123) by reaction with phosphoryl chloride and potassium selenosulphate[126], are rather unstable, but may be reacted with sodium sulphide and potassium ferricyanide to form 1,6-dithia-6aλ^4-selenapentalenes (239)[126]. The advantages in using the selenosulphate anion to introduce the selenium instead of the selenide or hydrogen selenide

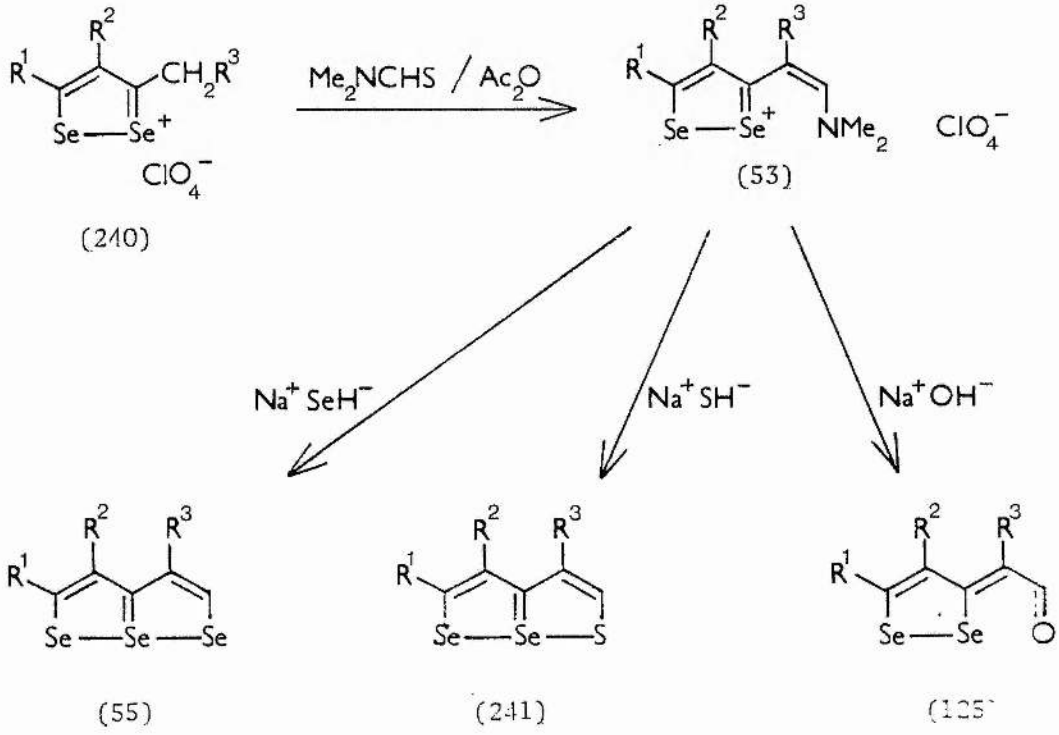
anions have been discussed in Section 1.A.6)a).



(123) (124) (239)

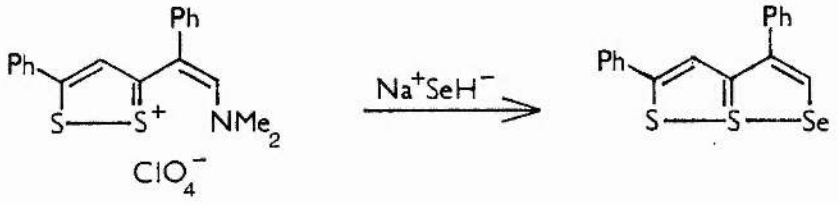
3) From 3-Alkyl-1,2-Diselenolium Salts

3-Alkyl-1,2-diselenolium perchlorates (240) react with N,N-dimethylthioformamide in acetic anhydride to form 3-(2-dimethylaminovinyl)-1,2-diselenolium perchlorates (53)[68] by virtue of the acidity of the methyl(ene) group adjacent to the ring. These versatile compounds may be reacted with sodium hydrogen selenide, sodium hydrogen sulphide, and sodium hydroxide to form the selenium-containing triheterapentalenes (55), (241), and (125)[68].



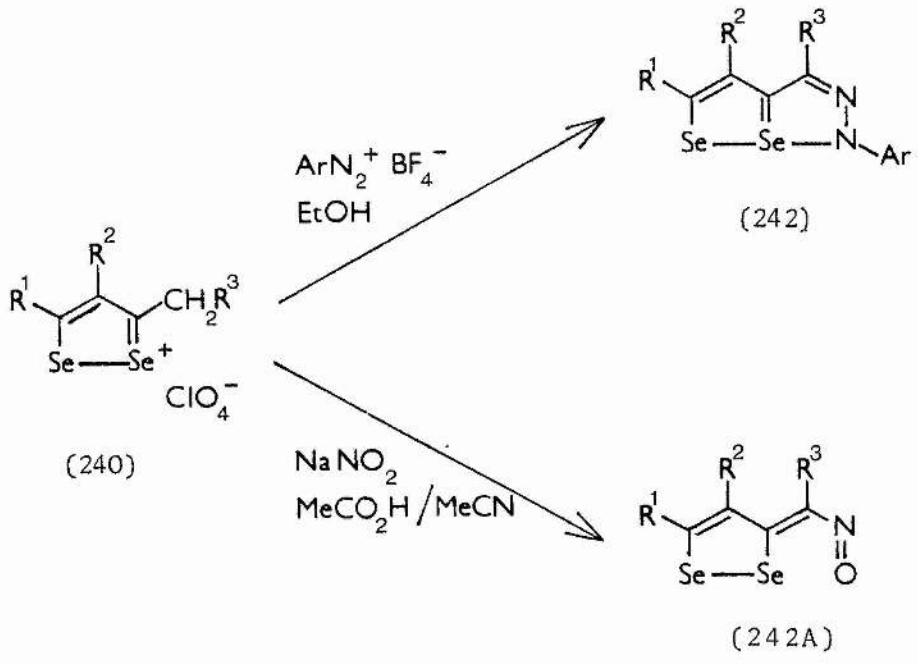
(240) (53) (55) (241)

The analogous 1,2-dithiolium perchlorate (54) may be reacted with sodium hydrogen selenide in a similar manner to obtain the 1,6aλ^4-dithia-6-selenapentalene (56)[75].



(54) (56)

3-Alkyl-1,2-diselenolium perchlorates (240) also afford heterapentalenes (242) and (242A) directly, when reacted with arenediazonium salts[208], and sodium nitrite in acetic acid[207], respectively.



4) From Other 1,6,6aλ^4-Triheterapentalenes

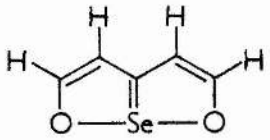
There are many different types of selenium-containing 1,6,6aλ^4-triheterapentalenes that may be formed from other triheterapentalenes, and many reagents have been used in the process[68,73,98,206,245,246]. These reactions offer great potential for the synthesis of new selenium-containing triheterapentalenes, but often require vigorous reaction conditions and afford several different products, thereby hindering the isolation and purification of any one desired product.

D. Reactions Of Selenium-Containing 1,6,6aλ^4-Triheterapentalenes And Related Systems

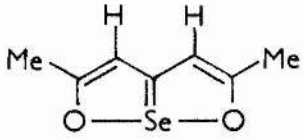
Comparatively little work has been carried out in this area apart from that discussed in Section 3.C.4), where one selenium-containing triheterapentalene was converted into another. However, the protonation of 1,6-dioxa-6aλ^4-selenapentalenes has been examined[247].

1) Protonation Of 1,6-Dioxa-6aλ^4-selenapentalenes

The ^{1}H n.m.r. spectra in trifluoroacetic acid of compounds (243) and (244) were examined, but no signs of protonation were apparent. However, when deuterated trifluoroacetic acid was used, the signals corresponding to the H_3 and H_4 protons disappeared, and the signal assigned to the H_2 and H_5 protons in compound (243) collapsed to a singlet, indicating that H - D exchange had occurred at the sites C_3 and C_4.



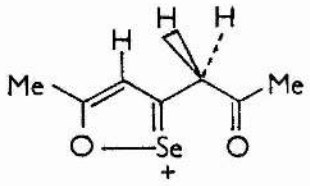
(243)



(244)

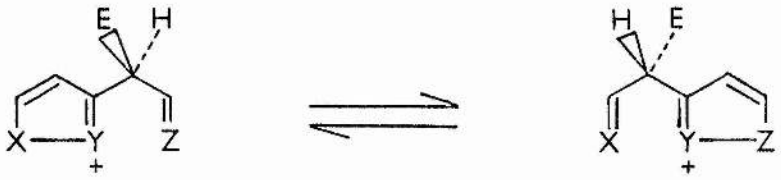
When 5% v/v perchloric acid/trifluoroacetic acid was employed as the n.m.r. solvent, compound (243) was destroyed, but the ^{1}H n.m.r. spectrum of compound (244) indicated that protonation to afford the cation (245) had occurred, since there was non-equivalence of the methyl signals, and a two-proton singlet at δ 5.10 ppm, corresponding

to the protonated site, had appeared.



(245)

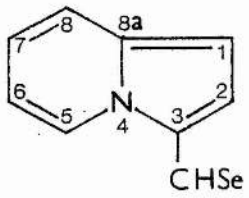
This evidence lends further weight to the general proposal[223] that electrophilic substitution of 1,6,6aλ^4-triheterapentalenes proceeds via an intermediate 6 π-electron monocyclic cation, although it does not distinguish between structures (246) and (247), which may be in equilibrium.



(246) (247)

4. Indolizine-3-Carboselenaldehydes

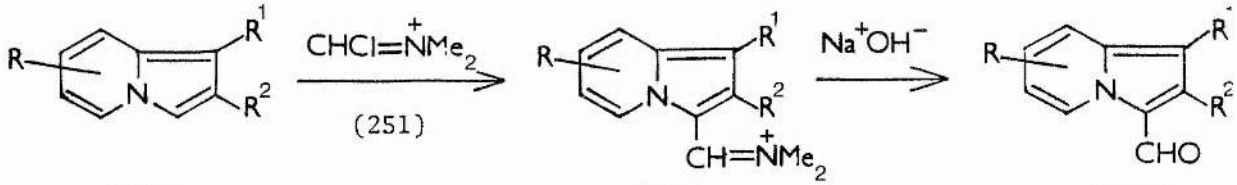
Since the work discussed in this thesis incorporated reactions with compounds containing the indolizine ring system, it is appropriate to discuss those containing selenium, especially the indolizine-3-carboselenaldehydes (49)/(248).



(248)

However, it would first of all be sensible to briefly consider the indolizine-3-carbaldehydes (249), since these are the compounds used to react with the selenium reagents to produce the selenium-containing products.

The indolizine-3-carbaldehydes (249) are obtained from the corresponding indolizines (250) by treatment with the Vilsmeier reagent (251), which is produced by the reaction of N,N-dimethyl-formamide and phosphoryl chloride, to give the corresponding Vilsmeier salts (45). These are then reacted with aqueous sodium hydroxide to obtain the indolizine-3-carbaldehydes (249)[248-250].

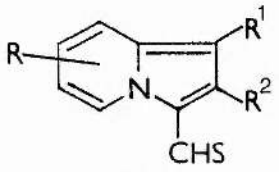


(250) (45) (249)

A. Structural Studies

1) Nuclear Magnetic Resonance Spectroscopy

The characteristic feature of the ^1H n.m.r. spectra of indolizine-3-carboselenaldehydes (49) is the low field signal, observed in the range δ 12.03 to 12.78 ppm[74], arising from the carboselenaldehyde proton. Indeed, this signal is deshielded by 1.6 to 2.0 ppm relative to the carbothialdehyde proton signal in the corresponding indolizine-3-carbothialdehydes (252).



(252)

It was also noted that if a 2-methyl substituent was replaced by a 2-t-butyl substituent, this low field signal experienced a further downfield shift of 0.3 to 0.5 ppm. This was attributed[74] to Van der Waal's deshielding of the carboselenaldehyde proton by the 2-t-butyl substituent.

The 3-carboselenaldehyde function exerts a strong diamagnetic anisotropic deshielding effect of approximately 4.0 ppm on the H_5 proton of the indolizine-3-carboselenaldehydes (49), as observed[74] when the relevant chemical shift values are compared with those of a suitable indolizine-1-carboselenaldehyde (50).

2) Miscellaneous Spectroscopic Techniques

Mass spectra of indolizine-3-carboselenaldehydes (49)[74] characteristically give rise to clusters of peaks corresponding to $RCHSe^{+\cdot}$ and $RCSe^{+}$, and to $RCH^{+\cdot}$ and RC^{+}, the latter cluster of peaks arising from the relatively facile loss of selenium from $RCHSe^{+\cdot}$ and $RCSe^{+}$.

The infra-red spectra of indolizine-3-carboselenaldehydes (49) are complex, but comparison with the spectra of analogous carbothialdehydes (252) enabled the stretching frequency of the C=Se bond to be identified[249] as being in the range 819 to 864 cm^{-1}. It was also noted that these limit values decreased slightly when the polarity of the solvent was increased.

The ultra-violet/visible spectra of indolizine-3-carboselenaldehydes (49) have been found[74] to be very similar to those of the corresponding carbothialdehydes (252), although the two broad absorption bands in the visible region occur at longer wavelength than in the carbothialdehyde analogues.

These techniques do not afford a great deal of structural evidence therefore, although spectral similarities of analogous carboselenaldehyde (49) and carbothialdehyde (252) compounds suggest that there may be similarities in the type of bonding present for each group of compounds.

B. Bonding

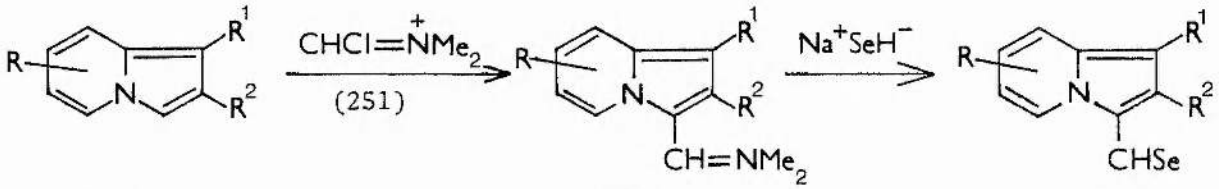
The most relevant feature of the bonding of indolizine-3-carboselenaldehydes (49) is that the indolizine system is quite strongly π-electron donating, and that conjugation with the carboselenaldehyde function is therefore possible, as indicated by the structural extremes (248) and (253).

(248) (253)

The resulting increase in the polarisation of the C=Se bond is promoted by the delocalisation of the positive charge into the indolizine ring. The carboselenaldehyde function is stabilised as a result, since the tendency to polymerise is correspondingly reduced.

C. Synthesis Of Indolizine-3-carboselenaldehydes

Indolizine-3-carboselenaldehydes (49) have been prepared from the Vilsmeier salts (45) of the corresponding indolizines (250)[74].

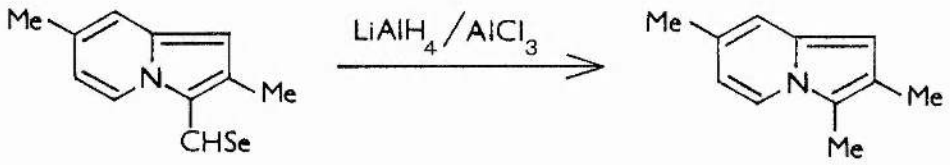


(250) (45) (49)

The indolizines (250) were treated with the Vilsmeier reagent (251), produced by the reaction of N,N-dimethylformamide with phosphoryl chloride, to produce the Vilsmeier salts (45). These were then reacted in situ with aqueous sodium hydrogen selenide to afford the indolizine-3-carboselenaldehydes (49), normally in moderate yields. However, in some cases, decomposition during purification considerably reduced the yields.

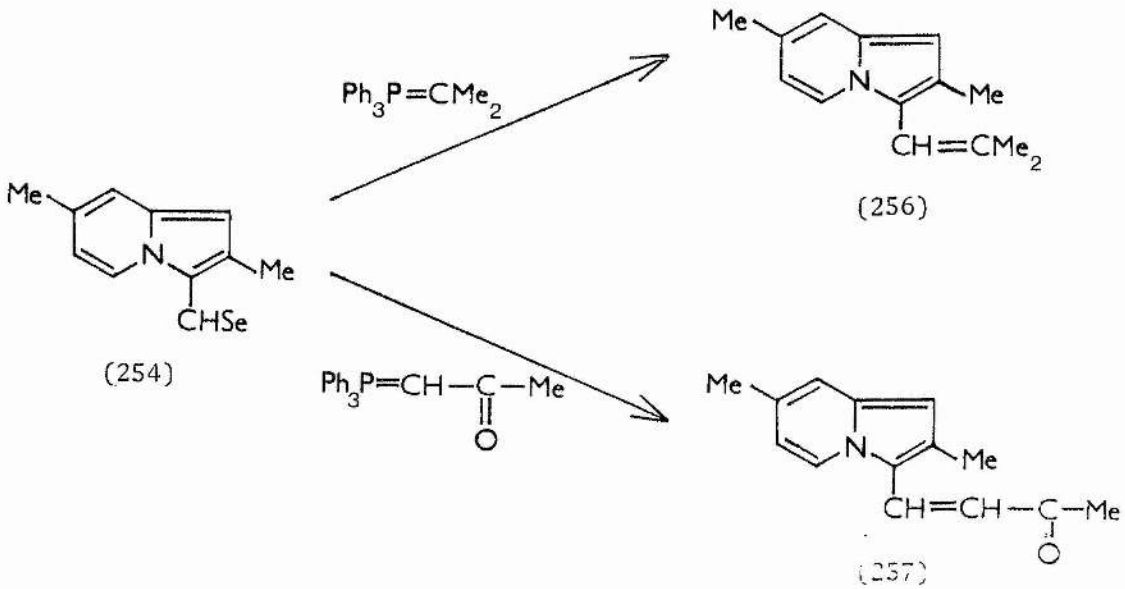
D. Reactions Of Indolizine-3-carboselenaldehydes

There are comparatively few examples of reactions involving indolizine-3-carboselenaldehydes (49), but they all indicate that the carboselenaldehydes react in a very similar manner to the analogous carbothialdehyde compounds (252). 2,7-Dimethylindolizine-3-carboselenaldehyde (254) was reduced by treatment with lithium aluminium hydride and aluminium chloride to afford 2,3,7-trimethylindolizine (255) in good yield[74].



(254) (255)

Compound (254) has also been utilised in Wittig reactions with isopropylidenetriphenylphosphorane and acetylmethylenetriphenylphosphorane, to afford 3-(2,2-dimethylvinyl)-2,7-dimethylindolizine (256), and 2,7-dimethyl-3-(3-oxobut-1-enyl)indolizine (257), respectively[74].



(254) (256)

(257)

PART B

DISCUSSION

1. Synthesis Of Selenium-Transfer Reagents

A. Synthesis Of Phenylphosphonoselenoic Dichloride (258)

Tervalent phosphines reacted smoothly with elemental selenium to afford substituted phosphine selenides, (see Introduction (Section 1.A.1)b)). This procedure was employed to prepare phenylphosphonoselenoic dichloride (258). Dichlorophenylphosphine (259) reacted with elemental selenium at temperatures of approximately 175°C, to give compound (258).

$$\underset{(259)}{PhPCl_2} + Se_x \xrightarrow{175\,^{\circ}C} \underset{(258)}{Ph\overset{\overset{Se}{\|}}{P}Cl_2}$$

A 20% excess of selenium was employed, and the residual selenium later weighed and the yield calculated. The reaction was found to proceed virtually quantitatively. The resulting product was dissolved in a predetermined volume of an appropriate solvent to obtain a stock solution of known molarity. This simplified ease of handling and use of the reagent during subsequent reactions. Despite the compound being sensitive to moisture and light, it could still be used after a period of one month, provided that it had been stored under nitrogen and in the dark.

Phenylphosphonoselenoic dichloride (258) was the first choice of reagent for the work embodied in this thesis, and was chosen for the following reasons. Previous experiments comparing the thionating reactivity of analogous phosphorus reagents[171] had indicated that chlorine substituents increased this reactivity. It was therefore

proposed that the presence of chlorine substituents in the chosen reagent would increase the selenating reactivity of the reagent. The phenyl substituent was chosen to provide a degree of stability to the reagent, so that it might be more easily handled.

B. Synthesis of Diphenylphosphonoselenoic Chloride (260)

In Section 1.A., it was proposed that the presence of chlorine substituents would increase the selenating reactivity of selenium-containing phosphorus(V) compounds. This was borne out when the synthesis of diphenylphosphonoselenoic chloride (260) from chlorodiphenylphosphine (261) was carried out. A comparable reaction procedure of heating the phosphine (260) with selenium afforded only some 67% of the desired reagent (260), along with 33% of the unreacted phosphine (261), after a comparable reaction time.

$$\underset{(261)}{Ph_2PCl} + Se_x \xrightarrow{185\ ^{\circ}C} \underset{(260)}{Ph_2\overset{Se}{\overset{\|}{P}}Cl}$$

The synthesis of this reagent was therefore not taken any further.

C. Synthesis of Tetramethylammonium Selenocyanate (262) And Its Reaction With Dichlorophenylphosphine (259)

It was proposed that an alternative method of producing a $\geqslant P{=}Se$ reagent might be to allow a selenocyanate to react with dichlorophenylphosphine (259). However, the readily available potassium selenocyanate (263) is hygroscopic, and it was therefore reacted with tetramethylammonium chloride (264) in refluxing acetonitrile to afford the non-hygroscopic tetramethylammonium selenocyanate (262).

$$\underset{(264)}{Me_4N^+Cl^-} + \underset{(263)}{K^+SeCN^-} \xrightarrow{\Delta} \underset{(262)}{Me_4N^+SeCN^-} + K^+Cl^- \downarrow$$

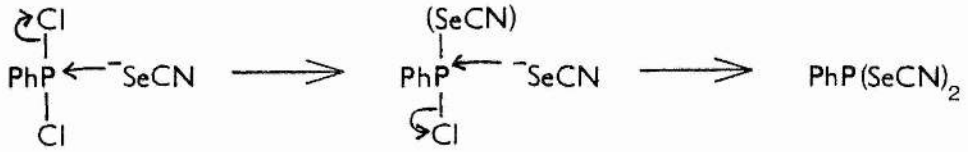
When an amount slightly in excess of two mole equivalents of tetramethylammonium selenocyanate (262) was reacted at ambient temperature in acetonitrile with dichlorophenylphosphine (259) under scrupulously dry conditions, the solution turned yellow, and a white solid was precipitated. If the slightest trace of moisture was present however, then immediate deposition of selenium occurred.

The precipitate was analysed by carbon-13 n.m.r., and the resulting spectrum indicated that only one environment of carbon was present, since a singlet signal was observed at δ 57.87 ppm[251]. This signal was split into a fine triplet, indicating the presence of a rotationally symmetrical nitrogen atom. The precipitate was tested for the presence of chloride ions using silver nitrate solution, and the test proved positive. A test for the presence of cyanide ions using ferrous sulphate solution, in case tetramethylammonium cyanide

had been formed, proved negative. These observations indicate that the white solid is tetramethylammonium chloride (264). This suggests that the reagent (265) is formed in acetonitrile under these reaction conditions, although to what extent is uncertain, for there may be an equilibrium present.

$$\underset{(259)}{PhPCl_2} + 2\ \underset{(262)}{Me_4N^+SeCN^-} \underset{?}{\rightleftharpoons} \underset{(265)}{PhP(SeCN)_2} + 2\ \underset{(264)}{Me_4N^+Cl^-}$$

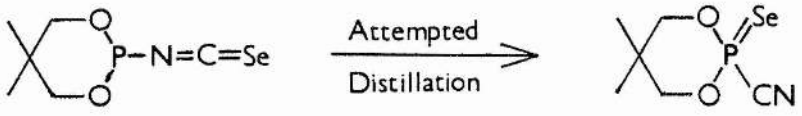
The proposed mechanism for this would involve the selenocyanate anion undergoing nucleophilic attack upon the phosphorus atom, thereby displacing a chloride anion. This would then be repeated to afford reagent (265).



(258) (265)

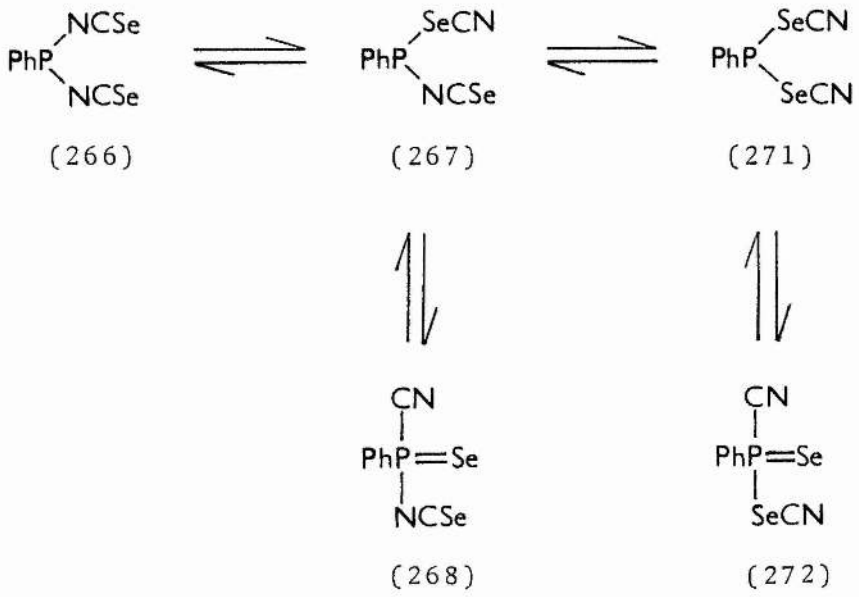
The selenocyanate anion is ambidentate however, and so could be bonded to the phosphorus atom through the selenium atom or the nitrogen atom. According to HSAB theory[252], the presence of chlorine substituents in phosphine (259) confers "hard" character upon the phosphorus atom, and so the reagent formed would perhaps be more likely to contain phosphorus-nitrogen bonds, rather than phosphorus-selenium bonds, and so might possess the structure (266), but with an equilibrium concentration of compound (267) present. This compound

may then undergo rearrangement to the energetically more favourable phosphorus(V) compound (268), thereby displacing the equilibrium between compounds (266) and (267) to the right. These proposals are consistent with the findings of Stec et al.[253], who describes the rearrangement of dialkylphosphoroisoselenocyanatidites (269) to dialkylphosphoroselenoates (270) upon attempted distillation.



(269) (270)

Other equilibria to form compounds (271) and (272) are also possible.



(266) (267) (271)

(268) (272)

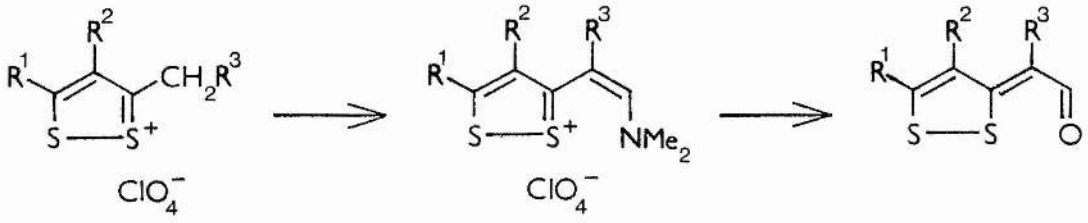
It was therefore proposed that compound (268) containing the P=Se

group may be formed in solution under the given reaction conditions, and that it may undergo oxygen-selenium exchange reactions *in situ* with carbonyl compounds.

2. Preparation Of Carbonyl Compounds

A. Preparation Of (1,2-Dithiol-3-ylidene)carbaldehydes (273)

The (1,2-Dithiol-3-ylidene)carbaldehydes (273 a-d) required in this study were prepared by established methods, from the corresponding 1,2-dithiolylium perchlorate salts (274), via the Vilsmeier salts (275)[75,207,220,223,254].



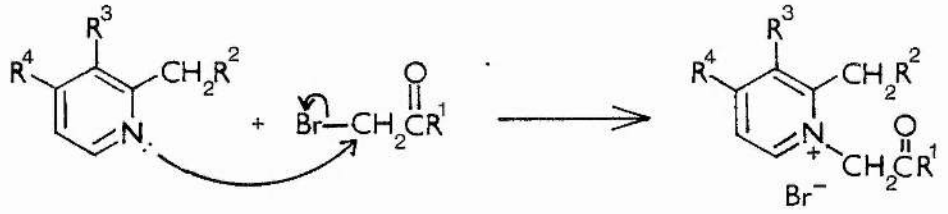
(274) (275) (273)

	R^1	R^2	R^3	References
a)	Ph	H	H	75
b)	t-Bu	H	H	220,223
c)	Ph	H	Me	75
d)	H	$-(CH_2)_3-$		207,254

B. Preparation Of Indolizine-3-carbaldehydes (276)

1) Preparation Of Pyridinium Bromide Salts (277)

Three pyridinium bromide salts (277) were prepared according to established methods, (277 a-c)[74,255]. In addition, salts (277 d-g) were synthesised by reaction of the appropriate pyridine (278) with 1-bromo-3,3-dimethylbutan-2-one (279 : R^1=Bu^t) in refluxing acetone.



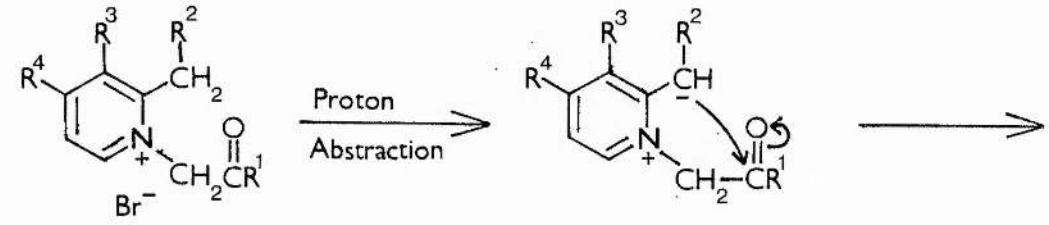
(278) (279) (277)

	R^1	R^2	R^3	R^4	References
a)	Me	H	H	Me	255
b)	t-Bu	H	H	Me	74
c)	t-Bu	Me	H	H	74
d)	t-Bu	H	Me	H	
e)	t-Bu	$-(CH_2)_2-$		H	
f)	t-Bu	$-(CH_2)_3-$		H	
g)	t-Bu	$-(CH_2)_4-$		H	

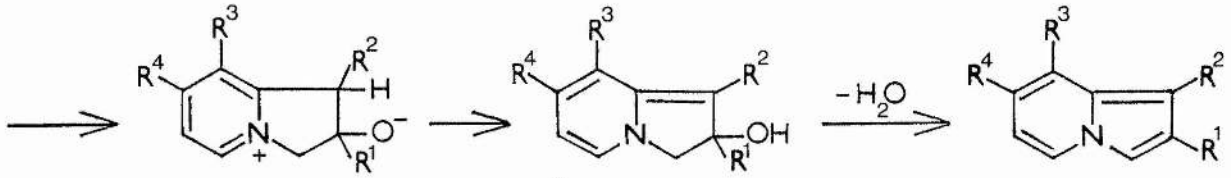
The relatively high melting points of these compounds, and their ease of solubility in water, were factors consistent with the structure (277). Compounds (277 d-g) were analysed, and found to be consistent with structure (277). The mass spectral data (Appendix 3) indicate an absence of molecular ion peaks which may be expected of a salt. The proton n.m.r. spectra exhibited all the appropriate signals, as did the carbon-13 n.m.r. spectra, including the distinctive carbonyl carbon signals between δ 206.48 ppm and 206.98 ppm. These signals have their shift values tabulated in Appendices 1 and 2 respectively.

2) Preparation Of Indolizines (280)

Indolizines (280 a-c) were prepared according to established procedures[74,255], while a further three indolizines (280 d,f,g) were synthesised by steam-distillation in the presence of sodium hydrogen carbonate. When the synthesis of indolizine (280e) was attempted however, no discernable product was obtained. It is suggested that this is because the ring strain induced by the cyclisation required to form the fused-ring system is too great to permit cyclisation to occur.



(277)



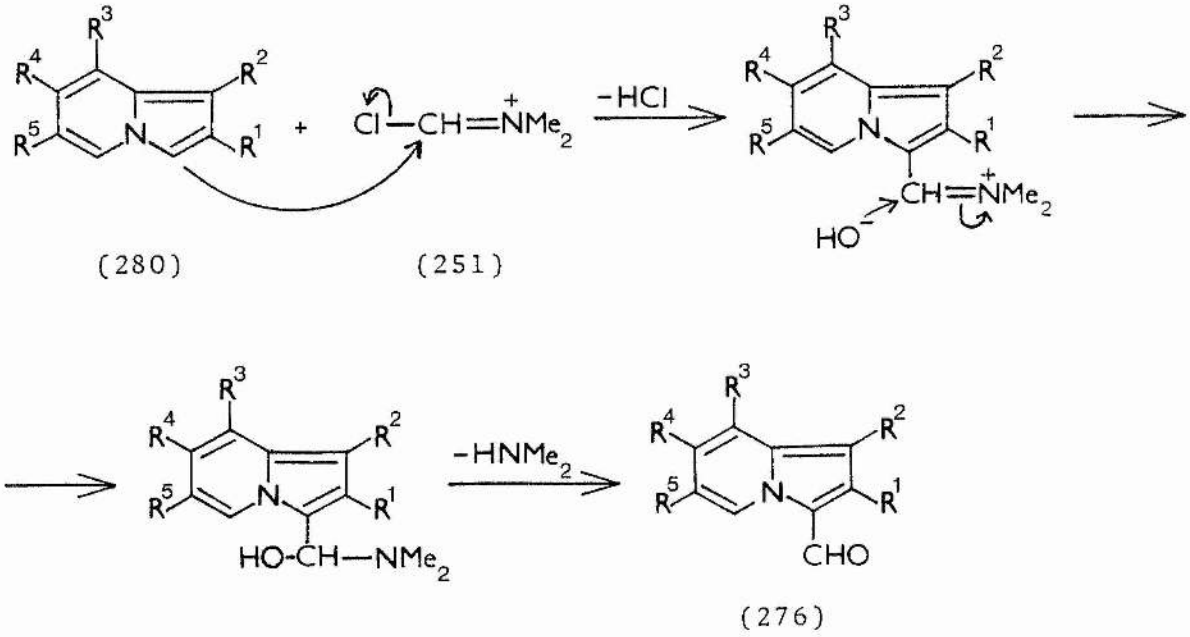
(280)

	R^1	R^2	R^3	R^4	References
a)	Me	H	H	Me	255
b)	t-Bu	H	H	Me	74
c)	t-Bu	Me	H	H	74
d)	t-Bu	H	Me	H	
e)	t-Bu	$-(CH_2)_2-$		H	
f)	t-Bu	$-(CH_2)_3-$		H	
g)	t-Bu	$-(CH_2)_4-$		H	

Indolizines (280) are usually relatively low melting compounds, and may sometimes be unstable in air. However, analyses carried out on compounds (280 d,f,g) were found to be consistent with the proposed structure. The mass spectral data (Appendix 3) indicate that the molecular ion peaks were present, but the n.m.r. spectra were not quite so informative as might have been expected, since the proton n.m.r. signals were not always completely resolved, whilst the downfield carbon-13 n.m.r. signals were often too weak to identify against the background noise. Nevertheless, assignments could be made in most cases, and are given in Appendices 1 and 2.

3) Preparation Of Indolizine-3-carbaldehydes (276)

Indolizine-3-carbaldehyde (276a) was prepared by established procedures[249].



(280) (251) (276)

	R^1	R^2	R^3	R^4	R^5	Reference
a)	Me	H	H	Me	H	249
b)	t-Bu	H	H	Me	H	
c)	t-Bu	Me	H	H	H	
d)	t-Bu	H	Me	H	H	
f)	t-Bu	$-(CH_2)_3-$		H	H	
g)	t-Bu	$-(CH_2)_4-$		H	H	

Compounds (276 b-d,f,g) were synthesised by the Vilsmeier reaction of the appropriate indolizine bases (280) with the iminium salt (251), which was prepared from phosphoryl chloride and N,N-dimethylformamide, at ambient temperature. The resulting Vilsmeier salts (281), reacted to give the desired aldehydes (276 b-d,f,g) in good yield.

Several other indolizine-3-carbaldehyde compounds (276 h-l) were generously made available for carbon-13 n.m.r. samples by other workers. A wide variety of data was therefore available for evaluation.

	R^1	R^2	R^3	R^4	R^5
h)	Me	H	H	H	H
i)	t-Bu	H	H	H	H
j)	Me	Me	H	H	H
k)	Me	H	H	H	Me
l)	Me	H	Me	H	H

The mass spectra of compounds (276 b-d,f,g) all exhibit a molecular ion peak (see Appendix 3 for data). The proton n.m.r. spectra of all the carbaldehyde compounds (276) (Appendix 1) indicate that the carbaldehyde proton signal is to be observed between δ 10.17 ppm and 10.34 ppm, and that the H_5 proton (H_4 in the case of compounds (276 f,g)) is characteristically observed between δ 9.68 ppm and 10.02 ppm. These latter signals are considerably further downfield than the

signals of the other ring protons, but upfield of the carbaldehyde proton signals.

The carbaldehyde carbon signals (Appendix 2) occur between δ 174.46 ppm and 178.53 ppm, and the $^{1}J_{C-H}$ coupling constants occur between 169.6 Hz and 174.3 Hz. With the exception of compound (276g), the signals corresponding to the C_1 carbon atom (C_{9a} in the case of compound (276f)) are to be found further upfield than the signals of all other ring carbon atoms, with $^{1}J_{C-H}$ coupling constants of between 172.8 Hz and 176.9 Hz where appropriate. However, the largest $^{1}J_{C-H}$ coupling constant is characteristically observed for the C_5 carbon atom (C_4 in the case of compounds (276f,g)) with values between 186.3 Hz and 191.8 Hz. In addition, apart from carbaldehyde (276k), this signal occurs further downfield than those of all the other unsubstituted ring carbon atoms. The $^{1}J_{C-H}$ coupling constants of the remaining ring carbon atoms occur in the range 160.3 Hz to 168.1 Hz, although they could not be measured for compound (276a).

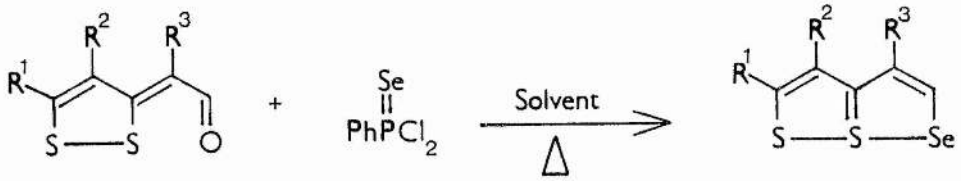
One final point to note regarding the carbon-13 n.m.r. data is the similarity in chemical shift values, and hence environment, of all the C_3 carbon atoms (C_2 in the case of compounds (276 f,g)), since the signals are observed between δ 120.14 ppm and 121.63 ppm, with the proviso that the signal was not observed for compound (276i).

3. Reactions Involving Selenium-Transfer Reagents.

A. Synthesis Of 1,6aλ^4-Dithia-6-selenapentalenes (282)

One member of this group of compounds has been previously prepared, 2,4-diphenyl-1,6aλ^4-dithia-6-selenapentalene (56)[75,98], and it was observed to be stable. It was therefore decided to prepare these compounds from the carbaldehydes (273) using phenylphosphonoselenoic dichloride (258).

The reaction of (1,2-dithiol-3-ylidene)carbaldehydes (273) with phenylphosphonoselenoic dichloride (258) was carried out under several different sets of conditions in order to find the most advantageous conditions.



(273) (258) (282)

	R^1	R^2	R^3
a)	Ph	H	H
b)	t-Bu	H	H
c)	Ph	H	Me
d)	H	$-(CH_2)_3-$	

Compound (273a) was used for this purpose. It was heated in benzene at reflux for fifteen minutes, in one experiment with a 150% excess of the reagent (258), in another with a 100% excess. It was found that with a 150% excess of the reagent (258), the yield of 1,6aλ^4-dithia-6-selenapentalene (282a) (45.6%) was greater than that obtained (42.1%) when only a 100% excess was used. It was therefore

decided to use a 150% excess of reagent (258) throughout these experiments.

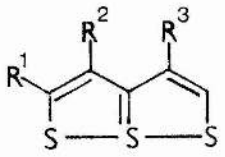
Other variables of the reaction conditions investigated were the reaction times and temperatures. It was considered possible that the temperature of refluxing benzene was too severe for the stability of these selenium-containing compounds, and so the experiment was carried out using dichloromethane as an alternative solvent. This lower reaction temperature meant that the reaction time had to be increased to ninety minutes. The yield of compound (282a) after work-up was found to be 50.5% - a slight improvement. It was therefore decided that all experiments be carried out in both benzene and in dichloromethane, in order to see if this result was general for the cases studied.

Compound (273b) was allowed to react with phenylphosphonoselenoic dichloride (258) in benzene, and also in dichloromethane. After identical reaction times to those previously employed, the mixtures were worked-up as before, and the results appeared to confirm those obtained for compound (273a), although the yield when using dichloromethane, 51.1%, was virtually identical to that obtained when using benzene, 50.5%.

The proposal was finally refuted when compound (273c) was treated in a similar fashion, since the yield of the reaction employing benzene was, at 70.2%, considerably better than that of the reaction using dichloromethane, 58.5%. It therefore seems that the conditions necessary for optimum yields vary from compound to compound, and they have to be determined individually.

The final reaction of this type involved the dithiole carbaldehyde (273d). This compound also gave an improved yield when reacted in dichloromethane (39.9%) as opposed to benzene (32.1%). The problem

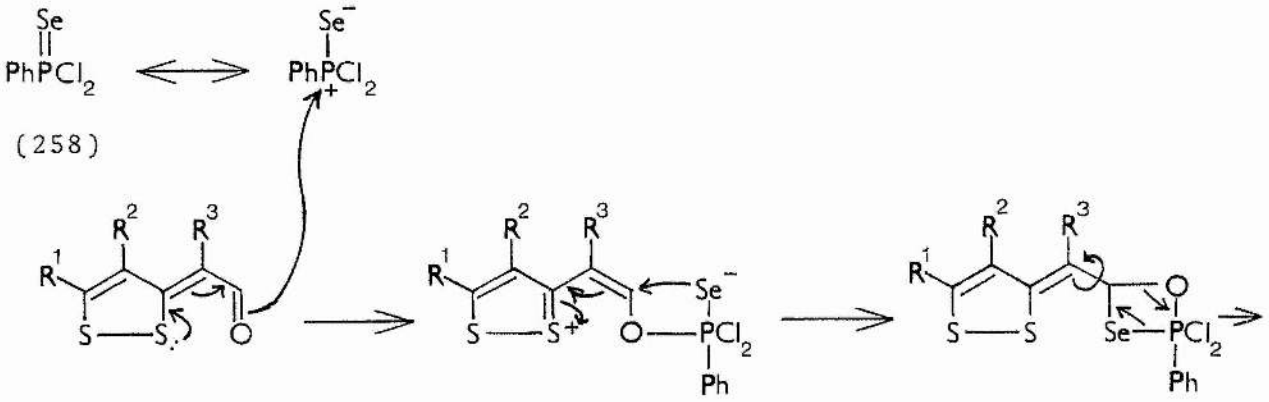
with this reaction was that the corresponding 1,6,6aλ^4-trithiapentalene (283d) was also formed during the course of the reaction, and it proved impossible to isolate the desired product (282d) from this impurity. The values stated for the yields are therefore for the combined yields of both compounds, and thus are not comparable with the previous reactions.



(283)

	R^1	R^2	R^3
d)	H	$-(CH_2)_3-$	

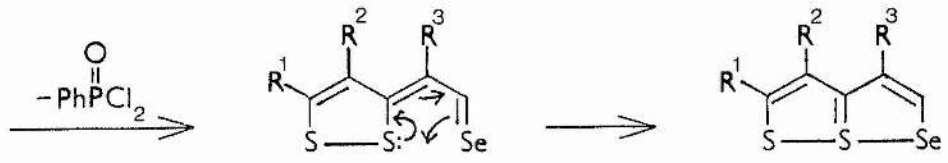
The mechanism postulated for these reactions involves a four-centre cyclic intermediate, as is the case in the Wittig reaction for the synthesis of alkenes.



(258)

(273)

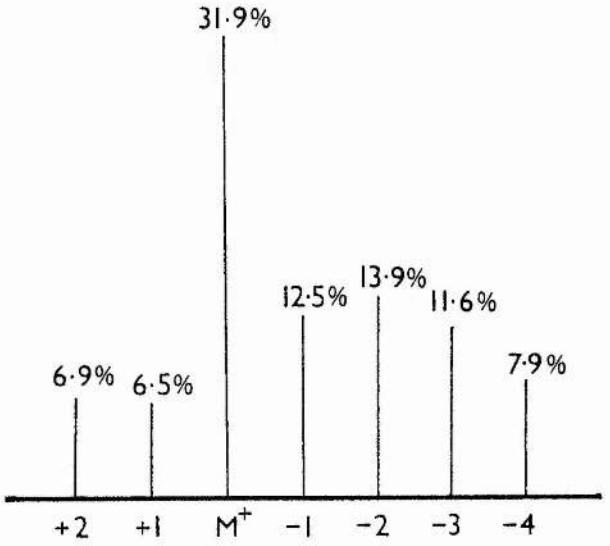
(284)



(282)

The phenylphosphonoselenoic dichloride (258) may be polarised as shown, and so the phosphorus atom may undergo nucleophilic attack by the carbaldehyde oxygen atom to give a four-centre cyclic intermediate (284). Loss of the corresponding phosphine oxide and subsequent cyclisation affords the 1,6aλ^4-dithia-6-selenapentalenes (282).

The resulting selenapentalenes (282) are highly coloured, purple crystalline solids, which show sharp melting points. The mass spectra of these compounds (282) showed a characteristic molecular ion cluster resulting from the presence of the various isotopes of selenium.



(282c)

This cluster indicates that not only are the isotopes of the molecular ion present, but so are those of the structure M^+-H. The mass spectral data are listed in Appendix 3.

The proton n.m.r. spectra (Appendix 1) show that the H_5 proton signals (H_6 in the case of compound (282d)) occur between δ 9.43 ppm and 10.23 ppm, and are therefore further downfield than the values for

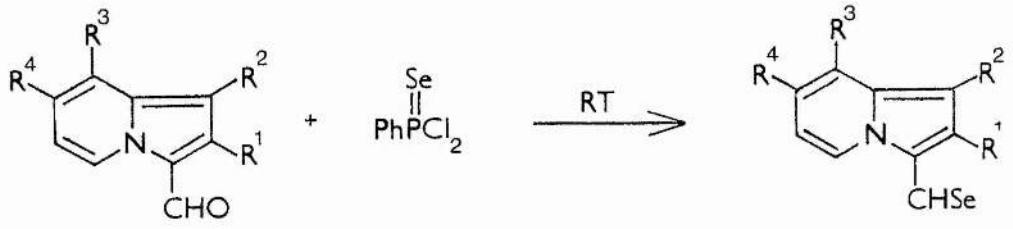
H_5 in the corresponding 1,6,6aλ^4-trithiapentalenes (283), which occur in the range δ 8.60 ppm to 9.36 ppm[75,256,207]. Other proton and substituent chemical shifts were observed to be only slightly further downfield compared with the trithiapentalenes (283). The proton n.m.r. spectrum of compound (282d) did indicate that the analogous trithiapentalene (283d) was present, thereby confirming the mass spectral and microanalytical evidence, which suggested that approximately 15% impurity of trithiapentalene (283d) was present.

The preparation of 1,6aλ^4-dithia-6-selenapentalenes (282) from carbaldehydes (273) using phenylphosphonoselenoic dichloride (258) was therefore successful. Compounds (282) were obtained in moderate to good yields, using a simple procedure and mild conditions.

B. Synthesis Of Indolizine-3-carboselenaldehydes (285)

Several indolizine-3-carboselenaldehydes (285 a-c,j) had been previously prepared directly from the corresponding indolizines (280 a-c,j) using aqueous sodium hydroxide[74]. The indolizine ring system was known to be a π-electron donor, and therefore to stabilise the carboselenaldehyde function. It was therefore decided to prepare these compounds using phenylphosphonoselenoic dichloride (258).

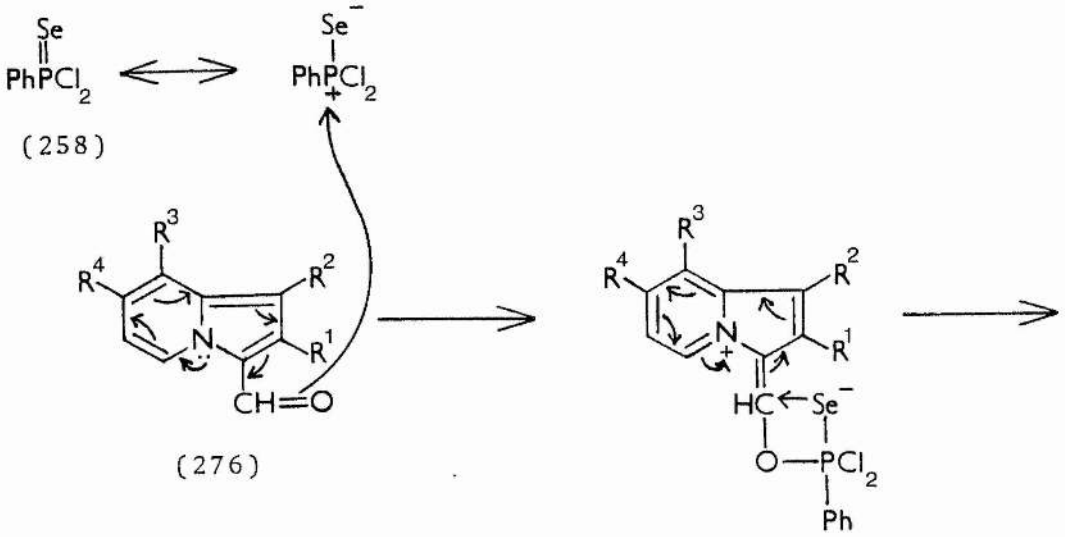
Indolizine-3-carbaldehydes (276 a-d,f,g) were allowed to react with a 50% excess of phenylphosphonoselenoic dichloride (258) in dichloromethane at ambient temperature for ten minutes. These mild conditions proved to be sufficient to bring about complete reaction of the carbaldehydes (276). The resulting reaction mixtures containing the carboselenaldehydes (285 a-d,f,g) were worked-up using as mild conditions as possible, and in reduced-light conditions, in an attempt to minimise the decomposition of the carboselenaldehydes (285).



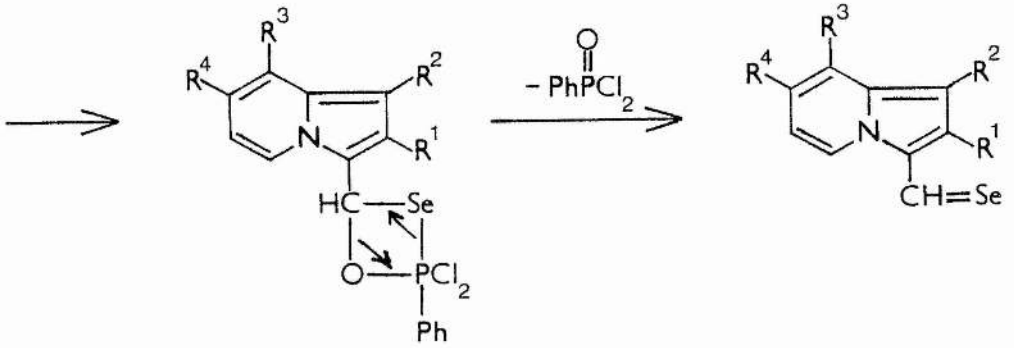
(276) (258) (285)

	R^1	R^2	R^3	R^4
a)	Me	H	H	Me
b)	t-Bu	H	H	Me
c)	t-Bu	Me	H	H
d)	t-Bu	H	Me	H
f)	t-Bu	$-(CH_2)_3-$		H
g)	t-Bu	$-(CH_2)_4-$		H
j)	Me	Me	H	H

The proposed mechanism is analogous to that described in Section 3.A., but with a different substrate.



(258) (276)



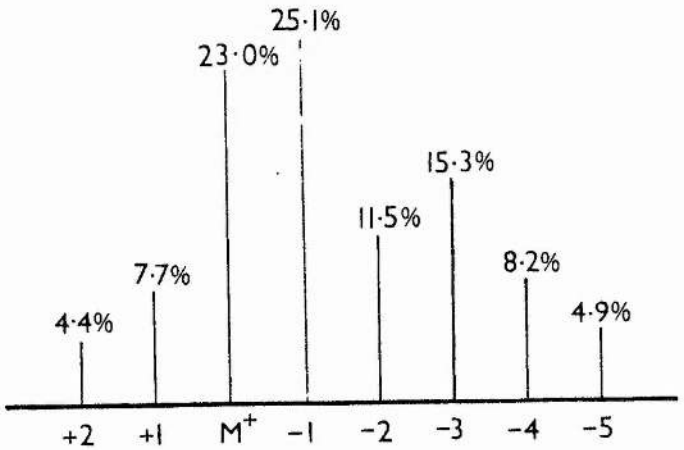
(286) (285)

Nucleophilic attack by the oxygen atom on the phosphorus atom produces the four-centre cyclic intermediate (286). Subsequent elimination of dichlorophenylphosphine oxide then affords the observed indolizine-3-carboselenaldehydes (285).

These carboselenaldehydes (285) are green in solution, and the

solids are highly coloured, ranging from ochre through green to purple in colour. Although the melting points appeared to be quite sharp, melting over a 2°C range at most, the compounds (285) appeared to decompose slightly a few degrees below the observed melting point. Yields varied between 31.8% and 72.4%, and may be compared with the yields obtained when the carboselenaldehydes (285) were prepared directly from the corresponding indolizines (280) using aqueous sodium hydrogen selenide as the reagent[74]. The yield of compound (285b) (72.4%) is significantly greater than previously obtained, even when the overall yield from the indolizine (280b) (62.6%) is considered. The yields of carboselenaldehydes (285 a,c) are slightly less than previously obtained[74], however. Therefore, although the reagent (258) is more efficient for preparing certain indolizine-3-carboselenaldehydes (285), it may not always be so.

The mass spectral data (Appendix 3) indicated that the molecular ion peaks due to the selenium isotopes were present. Often, as is the case for compound (285c) shown here, the M^+-H peak is the most intense in the molecular ion cluster.



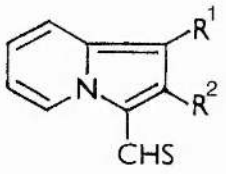
(285c)

The proton n.m.r. spectra of all the carboselenaldehydes (285) (Appendix 1), including compound (285j)[74], showed that the chemical shifts of the CHSe group occurred between δ 12.09 ppm and 12.78 ppm. These signals are far downfield when compared with those of the CHS group in the corresponding carbothialdehydes (287), which occur between δ 10.38 ppm and 10.95 ppm[248], and those of the CHO group in the carbaldehydes (276), which occur between δ 10.17 ppm and 10.34 ppm. The chemical shifts of the H_5 protons (H_4 in the case of compounds (285 f,g)) are comparatively far downfield when compared with other ring protons, and occur in the range δ 11.80 ppm to 12.36 ppm. These signals appeared upfield of the carboselenaldehyde proton signals in all of the cases examined. This parallels the observations made regarding indolizine-3-carbaldehydes (276).

The solubilities of the carboselenaldehydes (285) in deuterated trichloromethane was poor, and saturated solutions, often considerably less than 0.4M, were used. Indeed, the compound (285g) was also run in deuterated dichloromethane, giving very similar chemical shift values, but proving to be no more suitable with regards to solubility. Consequently, attempts to obtain carbon-13 n.m.r. spectra proved difficult, (see Appendix 2), and it sometimes proved impossible to observe all the quaternary carbon signals (285c), or even obtain a spectrum at all, (285g). Once again, deuterated dichloromethane was employed, but to no avail, for compounds (285 c,g). Compounds (285 a,b) did afford carbon-13 n.m.r. spectra in deuterated dichloromethane, but brought about no significant changes in the chemical shift values when compared with deuterated trichloromethane. When the n.m.r. spectra obtained when using deuterated trichloromethane were compared, it was noted that the chemical shift values of the carbo-

selenaldehyde carbon atoms were found to be in the range δ 176.79 ppm to 182.57 ppm. The corresponding $^1J_{C-H}$ coupling constants were relatively constant between 162.5 Hz and 163.0 Hz. When these values are compared with the corresponding values for indolizine-3-carbaldehydes (276), it may be seen that the signals are moved to lower field by between 1.32 ppm and 5.29 ppm, whilst the $^1J_{C-H}$ coupling constants are decreased by between 6.9 Hz and 10.1 Hz.

Two indolizine-3-carbothialdehydes (287 c,j)[248,249] were analysed by carbon-13 n.m.r. spectroscopy for comparison purposes.



(287)

	R^1	R^2	References
c)	Me	t-Bu	249
j)	Me	Me	248

They were analysed in both deuterated dichloromethane and trichloromethane, although compound (287c) proved to be not very soluble in deuterated dichloromethane, and so did not give a very good spectrum. The chemical shifts did not alter very much upon changing the n.m.r. solvent, although the carbothialdehyde carbon signal moved downfield by over 1 ppm in both cases when deuterated dichloromethane was employed. However, for the purposes of comparison, the data obtained when deuterated trichloromethane was employed will be discussed.

The carbothialdehyde carbon signals were observed at δ 182.29 ppm

and 186.15 ppm, and the corresponding $^{1}J_{C-H}$ coupling constants were 161.3 Hz and 162.0 ppm respectively. These values are such that the signals of the analogous carboselenaldehydes (285 c,j) appear between 7.65 ppm and 8.02 ppm further upfield than those of compounds (287 c,j), whilst the $^{1}J_{C-H}$ coupling constants are between 1.0 Hz and 1.2 Hz greater.

It might have been expected that when the chemical shift values of compounds (276), (287) and (285) were compared, a progressive downfield shift of the aldehydic carbon atom signal would be observed. This is not the case however, and one explanation for this may be that two factors have to be considered, namely the bond length and the degree of polarisation. Admittedly, comparable carbon-oxygen, carbon-sulphur and carbon-selenium bonds become progressively greater in length[193], but at the same time, this reduces the ability of carbon to form multiple bonds with the heteroatom concerned, since there will be a poorer p-orbital overlap between the two atoms. However if the double bond character is reduced by conjugation with a suitable electron-releasing group, then the bond will be stabilised. Such an electron-releasing group is the indolizine system, and it is proposed that the above occurs to some extent in the case of indolizine-3-carboselenaldehydes (285). Since it has been noted that the aldehydic function will be more shielded if polarised in this manner[248], this is a possible explanation for the fact that the carboselenaldehyde carbon signals appear upfield of those of the analogous carbothialdehydes (287).

Returning to the carbon-13 n.m.r. spectra of the indolizine-3-carboselenaldehydes (285), several other facts may be noted. As was the case for the carbaldehydes (276), the signal corresponding to the

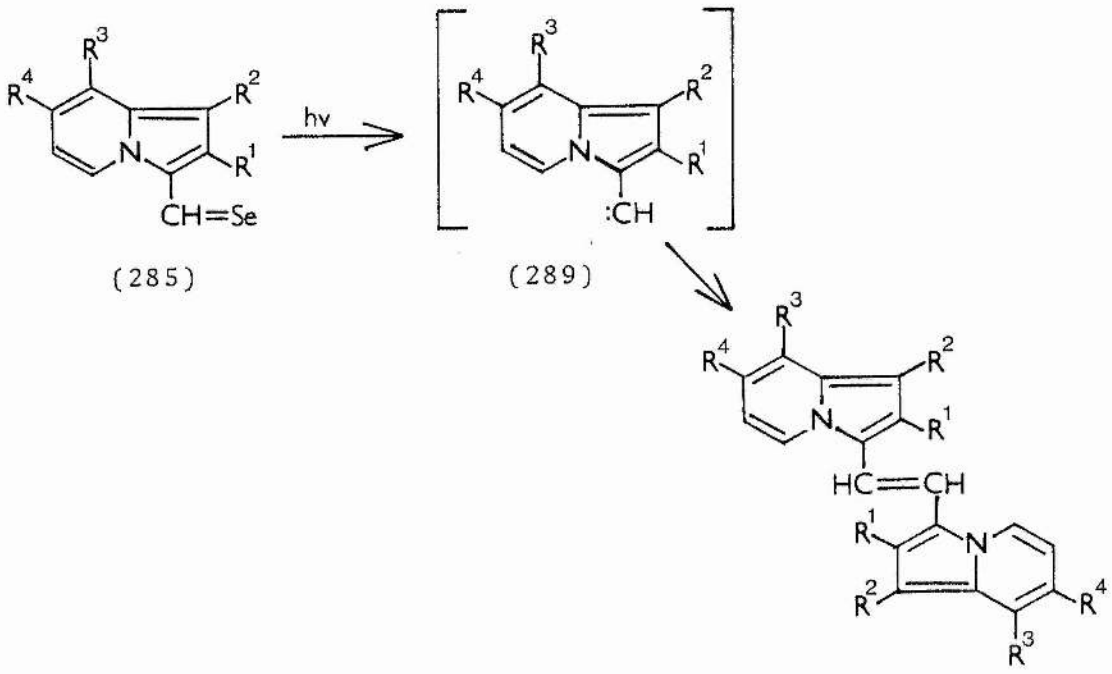
C_1 carbon atom (C_{9a} in the case of compound (285f)) occurs furthest upfield of all the ring carbon signals, this time without exception, for the compounds studied. Corresponding $^1J_{C-H}$ coupling constants are between 170.8 Hz and 174.6 Hz in magnitude, where appropriate. The largest $^1J_{C-H}$ coupling constants are again characteristically displayed by the C_5 carbon atom (C_4 in the case of compound (285f)), being between 185.0 Hz and 190.0 Hz where observable. However, this carbon atom is no longer the furthest downfield of the unsubstituted ring carbon atoms - this distinction is held by the C_7 carbon atom (C_6 in the case of compound (285f)) for these compounds. Where the remaining ring carbon atom $^1J_{C-H}$ coupling constants have been measurable, they have been found to be between 163.3 Hz and 167.9 Hz.

The chemical shifts of the signals corresponding to the ring carbon atoms with the carboselenaldehyde substituents are relatively constant, varying between δ 141.98 ppm and 143.78 ppm. Unfortunately, this signal was not observed for compound (285c).

In all the reactions of indolizine-3-carbaldehydes (276) with phenylphosphonoselenoic dichloride (258), a yellow side-product was produced during work-up. There was noticably more of the side-product in the reaction involving the carbaldehyde (276c), and this yellow compound was isolated, and obtained as a golden oil. Mass spectral (Appendix 3) and microanalytical data indicated that it was the 1,2-di-(indolizin-3-yl)ethene (288c). The desired product (285c) was therefore sufficiently unstable so as to undergo deselenisation and ultimately, to form some of the compound (288c). The compound (288c) accounted for 46.4% of the starting carbaldehyde (276c).

One possible mechanism leading to these side-products may involve the formation of a carbene intermediate (289), since desulphurisation

reactions to form carbenes in the presence of phosphorus compounds have been previously postulated[257]. Two such carbenes (289) might then react to form the compound (288). This was not investigated any further however, and so the intermediacy of a carbene (289) is hypothetical.



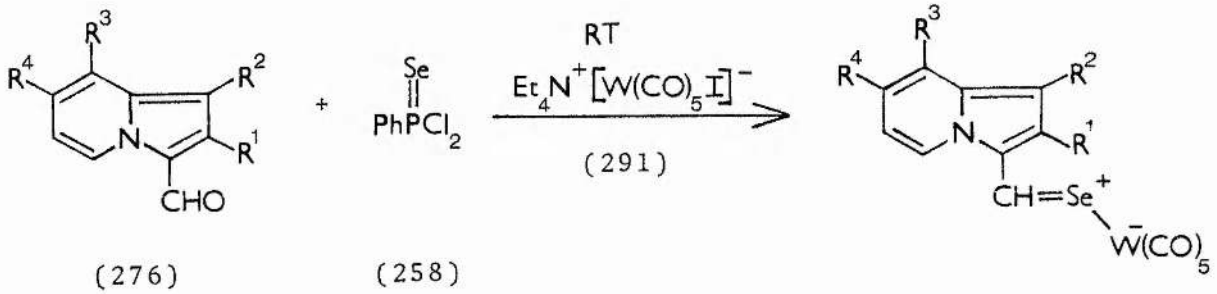
(285) (289) (288)

The reaction of indolizine-3-carbaldehydes (276) with phenylphosphonoselenoic dichloride (258) successfully produces the carboselenaldehydes (285) in moderate to good yields under mild reaction conditions. The yields obtained are comparable or better than those achieved by the preparation of indolizine-3-carboselenaldehydes (285) directly from indolizines (280) using sodium hydrogen selenide.

C. Synthesis of Pentacarbonyl(indolizine-3-carboselenaldehyde-Se)-tungsten(0) Complexes (290)

It was proposed in Section 3.B., that the indolizine-3-carboselenaldehyde system (285) is partially polarised in the sense $R^{+}=CH-Se^{-}$ in order to achieve stabilisation. It was therefore decided to utilise the proven ability of tetraethylammonium pentacarbonyliodotungstate(0) (291) to form pentacarbonyltungsten(0) complexes with organic substrates[258], to prepare a complex with the carboselenaldehydes (285) which would increase the stabilisation of the carboselenaldehyde function.

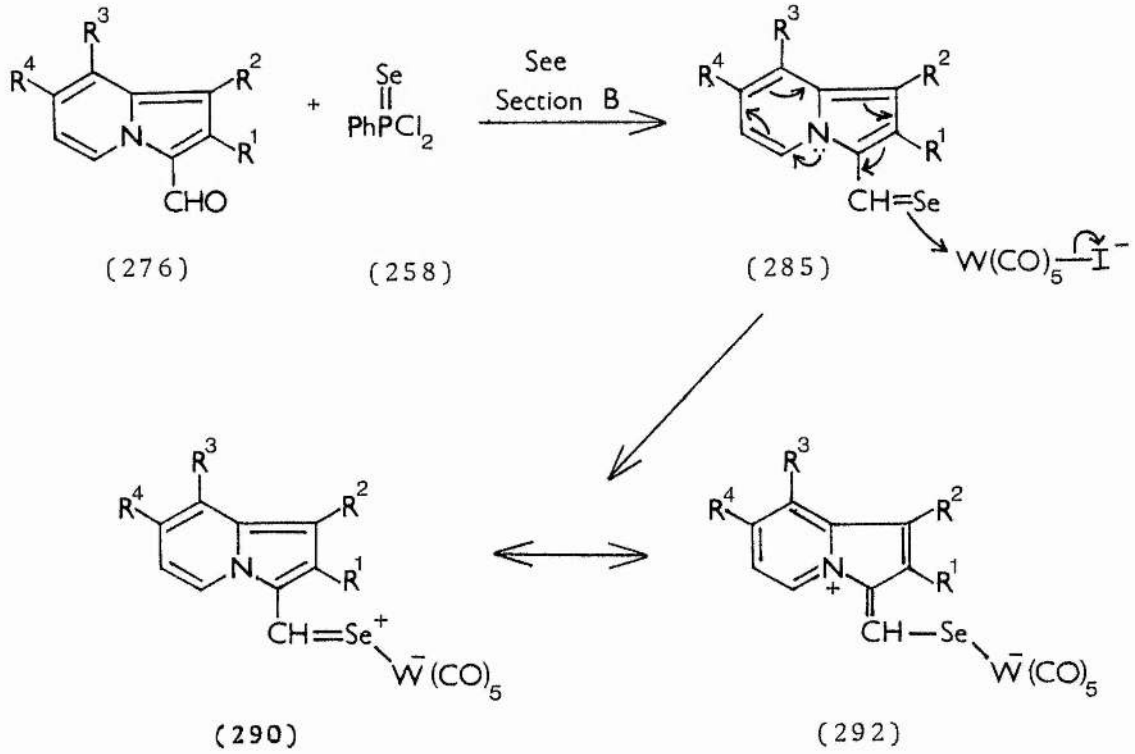
Indolizine-3-carbaldehydes (276) were therefore treated with phenylphosphonoselenoic dichloride (258) in dichloromethane in the presence of tetraethylammonium pentacarbonyliodotungstate(0) (291). Subsequent work-ups were carried out employing as mild conditions as possible, and in reduced-light conditions, in order to minimise decomposition of the desired pentacarbonyl(indolizine-3-carboselenaldehyde-Se)tungsten(0) complexes (290).



(276) (258) (290)

	R^1	R^2	R^3	R^4
a)	Me	H	H	Me
b)	t-Bu	H	H	Me
c)	t-Bu	Me	H	H
d)	t-Bu	H	Me	H
f)	t-Bu	$-(CH_2)_3-$		H
j)	Me	Me	H	H

The proposed mechanism involves the attack by the oxygen atom of the indolizine-3-carbaldehyde (276) on the phosphorus atom of the phenylphosphonoselenoic dichloride (258) as discussed in Section 3.B.. The resulting indolizine-3-carboselenaldehyde (285) may then undergo a S_N2 displacement reaction with the pentacarbonyliodotungsten(0) anion. The resulting complex (290) will be stabilised by the fact that the positive charge may be delocalised throughout the system, as indicated by the two structural extremes (290) and (292).



(276) (258) (285) (290) (292)

The pentacarbonyl(indolizine-3-carboselenaldehyde-Se)tungsten(0) complexes (290) were obtained as black solids, many of which possessed a metallic green sheen. True melting points could not be obtained, since all the complexes (290) appeared to decompose between the temperatures 161°C and 171°C. The yields varied from 39.1% for complex (290d) to 63.0% for complex (290f). As might have been

expected, the molecular ion peaks were not observed in the mass spectra (see Appendix 3), but common features were the progressive loss of carbonyl groups, and the presence of clusters of peaks arising from the various isotopes of tungsten.

Complexes (290 a-d) were analysed by proton n.m.r., but gave spectra which were poorly resolved, due to the lack of solubility of the complexes. Carbon-13 n.m.r. spectra could not be obtained for any complex (290). Complexes (290 a-d,f,j) were therefore analysed in deuterated dichloromethane using a high-field n.m.r. spectrometer. Proton and carbon-13 n.m.r. spectra are tabulated in Appendices 1 and 2 respectively.

One interesting point arose when the various proton spectra of complex (290a) were compared. It was discovered that whilst altering the n.m.r. solvent had relatively little effect upon most signals, it influenced the carboselenaldehyde proton signal sufficiently for it to appear downfield of the H_5 proton signal when run in deuterated trichloromethane, but upfield of it when run in deuterated dichloromethane.

Although the carboselenaldehyde proton signals were observed to have chemical shifts in the range δ 10.67 ppm to 11.30 ppm, it appeared to be relevant that the signals of complexes (290 a,j) occurred at δ 10.67 ppm and 10.72 ppm respectively, and were upfield of the H_5 proton signals, whilst those of the other complexes (290 b-d,f) occurred between δ 11.04 ppm and 11.30 ppm, and were downfield of the H_5 proton signals (H_4 in the case of comlex (290f)). There would appear to be a correlation with the fact that complexes (290 a,j) have a 2-methyl substituent, whilst the others possess a 2-t-butyl substituent.

These signals are much further upfield than the analogous signals of the indolizine-3-carboselenaldehydes (285), even after allowing for the use of a different deuterated solvent. This observation is in accordance with the conclusion that the more polarised the aldehydic function, the more shielded the environment, and hence the further upfield the signal is observed[248]. This would be expected, since by the very nature of these complexes (290), the polarisation of the carboselenaldehyde function has been enhanced with respect to that of the carboselenaldehydes (285). Since, in general, the yields of the complexes (290) are greater than those of the carboselenaldehydes (285), this may indicate a greater stability of the system.

The $^{3}J_{W-H}$ coupling constants of the doublet signals arising from the interaction with the tungsten atoms were measured, and found to be between 3.84 Hz and 4.25 Hz.

Even allowing for the use of a different deuterated solvent, the chemical environments of the H_5 protons (H_4 in the case of the complex (290f)) appear to be shielded when compared with those of compounds (285), since the chemical shifts of the former compounds occur in the range δ10.71 ppm to 11.12 ppm, whilst those of the latter compounds occur between δ 11.50 ppm and 12.36 ppm. The only signal that is slightly anomalous is that of complex (290f), appearing at δ 11.12 ppm, for if it is excluded, the range reduces to δ 10.71 ppm to 10.88 ppm.

The carbon-13 n.m.r. spectra show two signals, corresponding to different quaternary carbon environments, which appear relatively far downfield. The further downfield signals occur in the range δ 202.77 ppm to 202.92 ppm, and are much less intense. As a result, the $^{1}J_{W-C}$ coupling constant arising from the interaction with the tungsten atoms

could only be detected for complex (290a), and was found to be 163.7 Hz. The more intense signals are observed between δ 199.29 ppm and 199.39 ppm, and the analogous coupling constants were detected and calculated for several of these compounds, (290 a-d), and were found to be constant at 127.6 Hz. The former signals were therefore assigned to the axial carbonyl group, whilst the latter were assigned to the equatorial carbonyl groups.

The chemical shifts of the carboselenaldehyde carbon atoms were found to occur between δ 169.81 ppm and 176.18 ppm. The limits of this range are slightly further upfield than those of the analogous signals of the carboselenaldehyde compounds (285), which occurred between δ 176.79 ppm and 182.57 ppm. This variation in the chemical shift would appear to be greater than might be expected simply as the result of changing the deuterated solvent, and may therefore be a further indication of enhanced polarisation of the carboselenaldehyde function in these complexes (290), with respect to those in compounds (285).

The signal corresponding to carbon atom C_1 (C_{9a} in the case of complex (290f)), was found to be the furthest upfield of all the quaternary carbon atoms in the indolizine ring, whilst the furthest downfield was once again carbon C_7 (C_6 in the case of complex (290f)), as it was for the carboselenaldehydes (285). Unfortunately, the $^1J_{C-H}$ coupling constants for these signals were not determined.

The chemical shift values of the signals corresponding to the ring carbon atoms with the carboselenaldehyde substituents are once more fairly constant. These signals are somewhat further downfield than those of the carboselenaldehyde compounds (285) however, since they occur between δ 145.05 ppm and 147.33 ppm. Notwithstanding the

change in the deuterated solvent, this alteration may be the result of the chemical environment being more deshielded as a consequence of the enhanced polarisation of the carboselenaldehyde function that has been previously referred to.

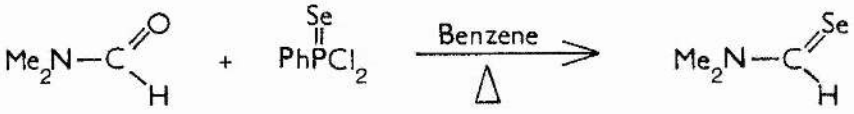
The complexes (290) are successfully prepared from indolizine-3-carbaldehydes (276) using phenylphosphonoselenoic dichloride (258) in the presence of tetraethylammonium pentacarbonyliodotungstate(0) (291). Mild reaction conditions were sufficient to achieve moderate to good yields of the complexes (290).

D. Synthesis Of Miscellaneous Selenocarbonyl Compounds

Since phenylphosphonoselenoic dichloride (258) had proved to be successful in introducing selenium into several classes of organic compounds, it was decided to allow this reagent (258) to react with various other carbonyl compounds.

1) Synthesis Of N,N-Dimethylselenoformamide (293)

N,N-Dimethylformamide (294) was allowed to react with a 100% excess of phenylphosphonoselenoic dichloride (258) in refluxing benzene for four hours. The work-up was conducted at ambient temperature where possible, and under reduced-light conditions throughout, to afford N,N-dimethylselenoformamide (293).

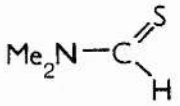


(294) (258) (293)

The proposed mechanism is analogous to that discussed in Section 3.B..

The resulting yellow oil was obtained in only 7.5% yield. Although a true boiling point was not obtained, the presence of selenoformamide (293) was confirmed by analytical data. Mass spectral data (Appendix 3) indicated that molecular ions corresponding to the various isotopes of selenium were present, and by the accurate mass calculations and microanalytical data which were in good agreement with calculated values.

Proton and carbon-13 n.m.r. spectra were also obtained, as were the carbon-13 n.m.r. spectra of N,N-dimethylthioformamide (295) and N,N-dimethylformamide (294) for comparison purposes. The data are given in Appendices 1 and 2 respectively. The proton n.m.r. spectrum in deuterated trichloromethane showed that the signal of the carboselenaldehyde proton occurs at δ 10.63 ppm, and the signals of the methyl substituents occurs at δ 3.35 ppm and 3.32 ppm. The literature values for the aldehydic protons of thioformamide (295) and formamide (294) are δ9.21 ppm and 8.02 ppm, respectively[259]. There is therefore a progressive downfield shift of the CHX signal in going from the carbaldehyde function to the carbothialdehyde function to the carboselenaldehyde function.

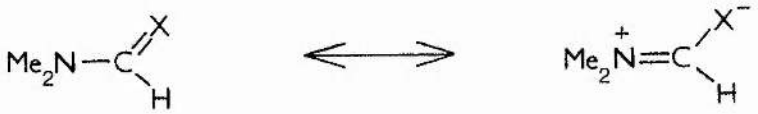


(295)

The trend is mirrored in the carbon-13 n.m.r. spectral data. The spectrum of N,N-dimethylselenoformamide (293) indicates that the carboselenaldehyde carbon atom signal occurs at δ 190.01 ppm, with an associated $^{1}J_{C-H}$ coupling constant of 177.6 Hz, and that signals corresponding to the carbon atoms of the methyl substituents appear at δ 47.39 ppm and 40.10 ppm. These values may be compared with those of compounds (295) and (294), which are δ 187.64 ppm, 45.23 ppm, 37.03 ppm, and δ 162.71 ppm, 35.99 ppm, 30.91 ppm, respectively. There is therefore a progressive downfield shift of the CHX signal in going from the carbaldehyde function to the carbothialdehyde function to the carboselenaldehyde function. The same trend apparently occurs for the

methyl signals.

All three compounds exhibit non-equivalence of the two methyl substituents with regard to chemical environment, as indicated by both proton and carbon-13 n.m.r. spectral data. It would therefore seem that these compounds are partially polarised, thereby restricting the rotation about the aldehydic carbon-nitrogen bond. The two methyl substituents would therefore no longer be experiencing the same chemical environment, and the shifts could not be averaged. However, averaging of the shifts may still occur if the temperature is raised sufficiently.



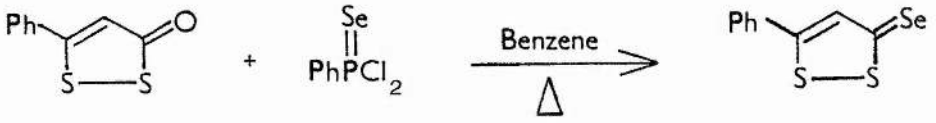
	X
(293)	Se
(295)	S
(294)	O

The use of phenylphosphonoselenoic dichloride (258) to convert N,N-dimethylformamide (294) directly to N,N-dimethylselenoformamide (293) has therefore proved to be only slightly less efficient than the use of phosphorus(V) selenide, which achieved a yield of 12%[101]. However, the selenoformamide (293) has been much more efficiently prepared from carbon diselenide, benzyl selenol and dimethylamine[260].

2) Synthesis Of 5-Phenyl-3H-1,2-dithiole-3-selone (296)

5-Phenyl-3H-1,2-dithiol-3-one (297) was reacted with a 100%

excess of phenylphonosphoselenoic dichloride (258) in refluxing benzene for twenty minutes to afford 5-phenyl-3H-1,2-dithiole-3-selone (296) in 7.6% yield. Reduced-light conditions were maintained throughout.



(297) (258) (296)

In an effort to improve this yield, the reaction was repeated in both toluene and in xylene to afford the compound (296) in 11.3% and 12.1% yields, respectively. The proposed mechanism is analogous to that discussed in Section 3.B..

The orange-brown needles that were formed had a melting point of 131°-132°C, and their analyses gave results which were in good agreement with calculated values. In the mass spectrum, molecular ion peaks resulting from the various isotopes of selenium were also observed, (Appendix 3). N.m.r. spectra were obtained, and were compared with the proton and carbon-13[261] n.m.r. spectra of the 1,2-dithiol-3-one (297) and the 1,2-dithiole-3-thione (298). Spectral data are given in Appendices 1 and 2 respectively.

The proton signals arising from the phenyl substituents occurred as complex multiplets, and at approximately the same chemical shift values, but the H_4 proton signals of compounds (298) and (296), which both occurred at δ 7.42 ppm, were observed to appear downfield with respect to the analogous signal for compound (297), which occurred at δ 6.83 ppm.

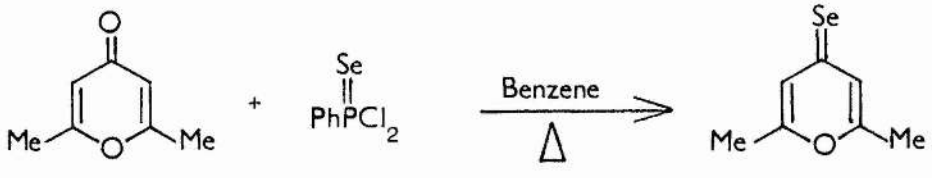
The chemical shift values obtained from the carbon-13 n.m.r.

spectrum of selone (296) were compared with the corresponding values of thione (298) and ketone (297). The value corresponding to carbon atom C_3 was δ193.90 ppm for compound (297), δ215.60 ppm for thione (298) and δ 247.73 for selone (296). This signal was the furthest downfield of any selenium-containing compound that was studied during the course of the work embodied in this thesis. This progressive downfield shift was also observed for the signals arising from carbon atoms C_5 and C_4. The chemical shift values of the carbon atoms of the phenyl substituents in these compounds were not significantly different.

Although 5-phenyl-3H-1,2-dithiole-3-selone (296) had been previously prepared[262], it was not obtained directly from the corresponding 1,2-dithiol-3-one (297), but rather from the reaction between 3-chloro-5-phenyl-1,2,dithiolylium chloride and N-phenylselenourea.

3) Synthesis Of 2,6-Dimethyl-4H-pyran-4-selone (299)

2,6-Dimethyl-4H-pyran-4-one (236) was allowed to react with a 100% excess of phenylphosphonoselenoic dichloride (258) in refluxing benzene for thirty minutes to afford 2,6-dimethyl-4H-pyran-4-selone (299) in only 1.3% yield. Reduced-light conditions were maintained throughout.



(236) (258) (299)

In an effort to improve upon this very poor yield, the reaction was repeated using toluene instead of benzene, but no product whatsoever was obtainable after work-up.

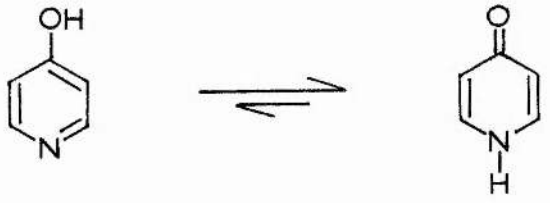
The proposed mechanism to afford the 4-H-pyran-4-selone (299) is analogous to that discussed in Section 3.B..

The poor yield of material obtained may be explained by the fact that 2,6-dimethyl-4H-pyran-4-selone (299) is known to be relatively unstable[73], and indeed, the thiopyran-4-selone has been described as being thermally unstable[263]. Therefore, it may be that the selone (299) is unstable at the reaction temperatures employed.

The red crystalline product was analysed by mass spectrometry only, and the data obtained is given in Appendix 3. This data indicated that the molecular ion cluster resulting from the isotopes of selenium was present, and the product was therefore identified using this information. This method of preparation was therefore not nearly as efficient as the two-stage process previously developed[73], that afforded the 4H-pyran-4-selone (299) from the corresponding 4H-pyran-4-one (236) in an overall yield of 65.7%.

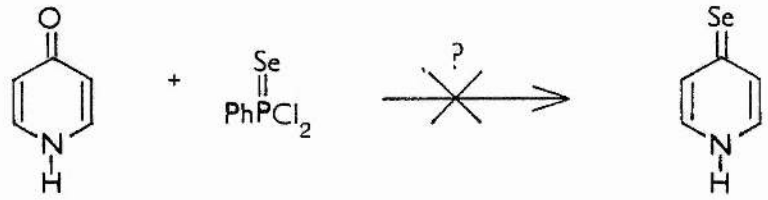
4) Attempted Synthesis Of 4(1H)-pyridineselone (300)

4-Hydroxypyridine (301) exists in equilibrium with its major tautomer 4(1H)-pyridinone (302), and was therefore proposed as a suitable substrate to react with phenylphosphonoselenoic dichloride (258).



(301) (302)

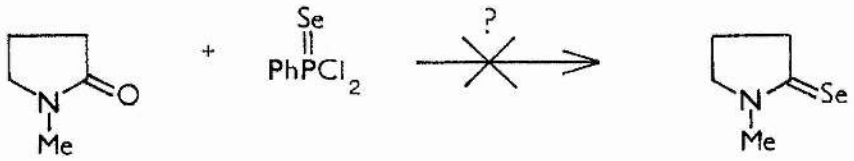
The reaction was carried out in refluxing acetonitrile for fifteen minutes, using a 100% excess of phenylphosphonoselenoic dichloride (258). Despite maintaining reduced-light conditions throughout, no discernable product was obtained. The reaction was then repeated at ambient temperature for two hours. On this occasion, a slight trace of material was observed, but deposition of selenium occurred, and no product could be obtained. No starting material was observed for either reaction.



(302) (258) (300)

5) Attempted Synthesis Of 1-Methylpyrrolidine-2-selone (303)

1-Methylpyrrolidin-2-one (304) was allowed to react with a 100% excess of phenylphosphonoselenoic dichloride (258) in refluxing benzene for two hours, under conditions of reduced light.



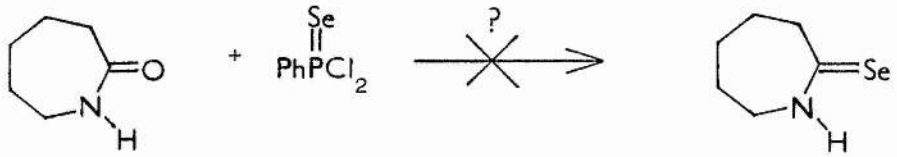
(304) (258) (303)

The reaction mixture was worked-up and chromatographed on alumina to afford pale yellow eluates which rapidly deposited selenium upon

concentration, preventing any characterisable product from being obtained. The reaction was then repeated under identical conditions, except that a silica column was used for chromatography. The pale yellow eluates that were collected rapidly deposited selenium as before, and so no product could be obtained.

6) Attempted Synthesis Of Hexahydro-2H-azepine-2-selone (305)

Hexahydro-2H-azepin-2-one (306) was allowed to react with a 100% excess of phenylphosphonoselenoic dichloride (258) in refluxing benzene for one hour. Despite the fact that reduced-light conditions were maintained throughout the reaction and subsequent work-up, the yellow eluates that were collected after chromatography rapidly deposited selenium upon concentration. No characterisable product could be obtained.

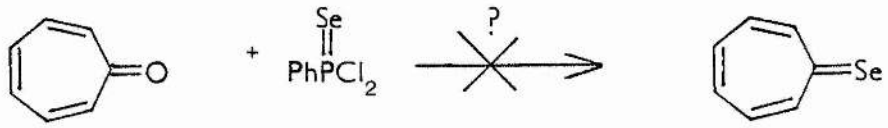


(306) (258) (305)

7) Attempted Synthesis Of 2,4,6-Cycloheptatriene-1-selone (307)

2,4,6-Cycloheptatrien-1-one (308) was allowed to react with a 100% excess of phenylphosphonoselenoic dichloride (258) at ambient temperature for one hour in benzene. Despite the reaction and subsequent work-up being carried out in an atmosphere of nitrogen, and

under reduced-light conditions, the white needles which were formed in the reaction mixture, and which were enhanced by the addition of ether, rapidly deposited selenium upon filtration. They also proved to be extremely hygroscopic, despite the fact that all the work-up was carried out in a purged dry-box. The reaction was repeated, with benzene employed during the work-up procedure instead of ether, but with no improvement. No characterisable product could be obtained from either reaction..



(308) (258) (307)

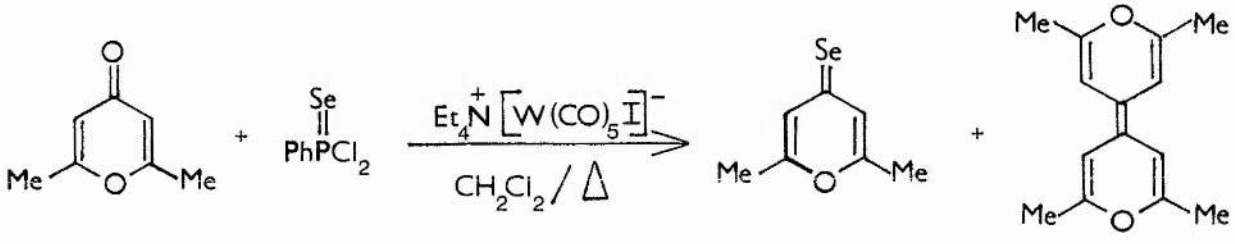
In general, the use of phenylphosphonoselenoic dichloride (258) to introduce selenium into these organic carbonyl compounds proved less successful than anticipated. This may be the result of the compounds being unable to donate π-electrons so as to stabilise the resulting carboselenaldehydes and selones sufficiently.

E. Synthesis Of Miscellaneous Pentacarbonyl(selone-Se)-tungsten(0) Complexes

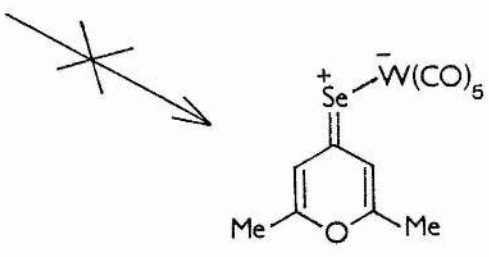
Tetramethylammonium pentacarbonyliodotungstate(0) (291) was introduced to attempt to trap the selones as the tungsten pentacarbonyl complexes.

1) Attempted Synthesis Of Pentacarbonyl(2,6-dimethyl-4H-pyran-4-selone-Se)tungsten(0) (309)

Phenylphosphonoselenoic dichloride (258) was allowed to react with 2,6-dimethyl-4H-pyran-4-one (236) in the presence of tetraethylammonium pentacarbonyliodotungstate(0) (291). A 50% excess of reagent (258) and a 10% excess of tungstate (291) were employed, and the mixture heated at reflux in dichloromethane for fifteen minutes. Although reduced-light conditions were maintained throughout, the subsequent work-up only afforded a 0.5% yield of a red crystalline product, believed to be a mixture of compounds (299) and (310).

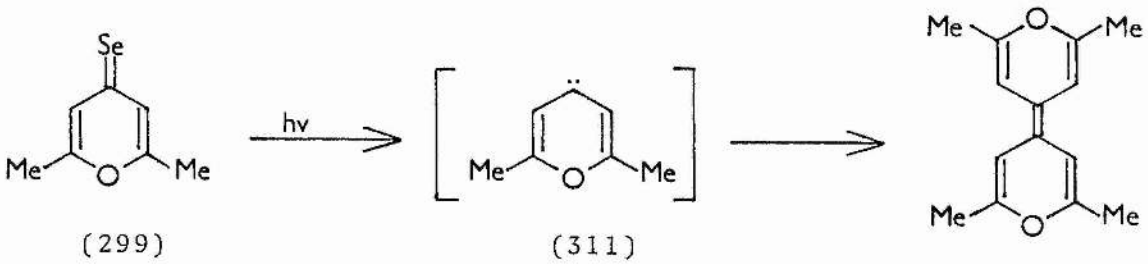


(236) (258) (299) (310)



(309)

Although the red crystalline product could be analysed by mass spectrometry only (details in Appendix 3), the spectrum clearly showed that the expected pentacarbonyltungsten(0) complex (309) had not been formed. Instead, the 4H-pyran-4-selone (299) was present, giving a cluster of molecular ion peaks at m/z = 188 etc.. This did not appear to be the only product, however, since the data indicated that compound (310) was also present. In a proposed mechanism analogous to that suggested in Section 3.B., the selone (299) may have undergone deselenisation to afford the carbene intermediate (311). Two such carbenes (311) may then react to give 2,2',6,6'-tetramethyl-4,4'-bi-pyranylidene (310). It is not understood why the tungsten complex was not formed.

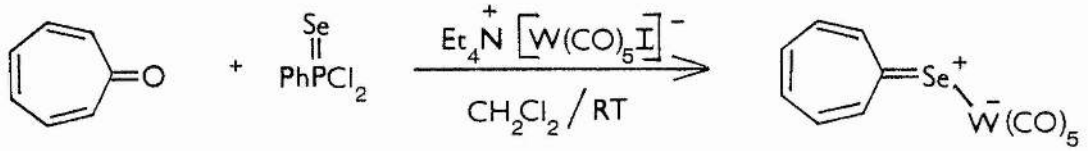


(299) (311) (310)

2) Synthesis Of Pentacarbonyl(2,4,6-cycloheptatriene-1-selone-Se)-tungsten(0) (312)

The reaction of phenylphosphonoselenoic dichloride (258) with 2,4,6-cycloheptatrien-1-one (308) in the presence of tetraethyl-ammonium pentacarbonyliodotungstate(0) (291) was carried out in an attempt to trap the selone (307) as the complex (312). A 50% excess of the reagent (258) and a 10% excess of the tungstate (291) were

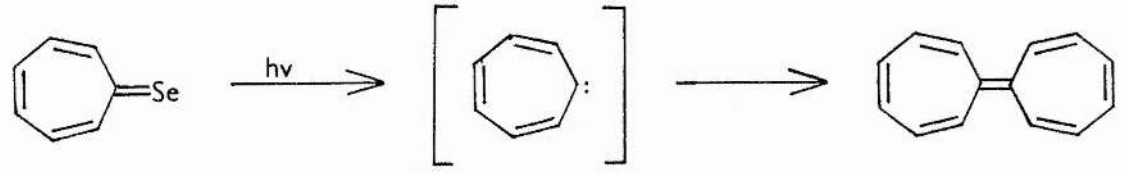
employed, and the mixture stirred at ambient temperature in dichloromethane for one hour. All procedures were carried out using reduced-light conditions, using an inert atmosphere. The subsequent work-up afforded a 4.4% yield of pentacarbonyl(2,4,6-cycloheptatriene-1-selone-Se)tungsten(0) (312), which was obtained as bronze micro-needles.



(308) (258) (312)

The proposed mechanism is analogous to that given in Section 3.C., namely that the selone (307) is formed, and then undergoes a S_N2 displacement reaction with the pentacarbonyliodotungstate(0) anion to afford the complex (312).

No molecular ion cluster was observed for the complex (312) in the mass spectrum (see Appendix 3), although peaks corresponding to isotopes of tungsten were observed, as were those arising from the progressive loss of carbonyl groups. The mass spectrum also appeared to indicate that the compound 1,1'-bicycloheptatrienylidene (313) was present. This compound may have been formed by the deselenisation of the selone (307) to afford the carbene intermediate (314). Two carbene intermediates could then react to form the compound (313).

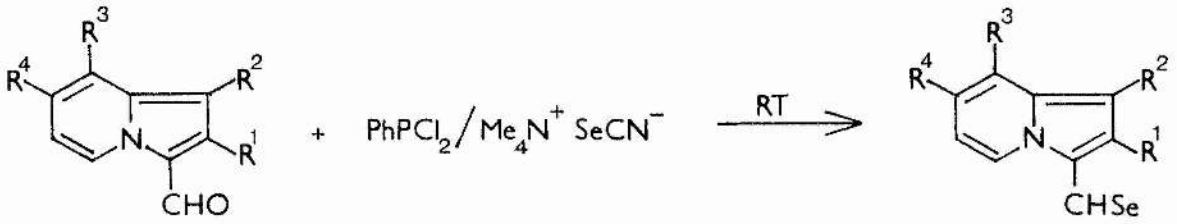


(307) (314) (313)

Unfortunately, the complex (312) proved impossible to purify to a sufficient standard for an acceptable microanalysis to be carried out, possibly as a result of the available selenium obtained from the deselenisation process. It also proved to have low solubility in deuterated solvents. A proton n.m.r. spectrum in deuterated dichloromethane was obtained by using a high-field spectrometer (Appendix 1), but a carbon-13 n.m.r. spectrum could not be obtained. Upon examination of the proton spectrum, it was noted that two signals, each corresponding to only one proton, appeared slightly downfield of the multiplet which represented the remaining four protons. These two signals presumably represent protons H_2 and H_7, thereby indicating a non-equivalence in the chemical environment of each, caused by the non-linearity of the C=Se-W three atom sequence.

F. Reaction Of Indolizine-3-carbaldehydes (276)
With The Reagent Formed By The Reaction
Of Phenyldichlorophosphine (259)
With Tetramethylammonium Selenocyanate (262)

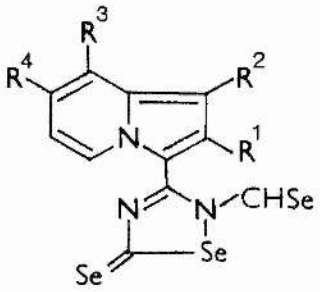
The reaction of dichlorophenylphosphine (259) with tetramethylammonium selenocyanate (262) was discussed in Section 1.C., where it was proposed that the reagent (268) is produced. This compound was not isolated, and was used *in situ*. Indolizine-3-carbaldehydes (276) were shown in Section 3.B. to be suitable substrates to react with phenylphosphonoselenoic dichloride (258), and so were introduced into a solution of this reagent (268) in acetonitrile, previously generated from phenyldichlorophosphine (259) and tetramethylammonium selenocyanate (262). In each case, the reaction mixture was stirred at ambient temperature for ten minutes, by which time the reaction had gone to completion. The subsequent work-up was carried out under reduced-light conditions to afford two main products, which were separated by extraction of the more soluble one into benzene. The more soluble products from these reactions were shown to be the indolizine-3-carboselenaldehydes (285 a-d,f,j), previously obtained by the reaction of the corresponding carbaldehydes (276) with phenylphosphonoselenoic dichloride (258). They were obtained in yields of between 19.7% and 43.9%, and where comparisons could be made, these yields were usually poorer than the yields of carboselenaldehydes (285) obtained from the reaction of carbaldehydes (276) with phenylphosphonoselenoic dichloride (258). The only observed exception involved compound (285c), since the yield obtained (33.3%), was greater than the yield obtained in the reaction involving phenylphosphonoselenoic dichloride (258), (31.8%).



(276) (259) / (262) (285)

+

	R^1	R^2	R^3	R^4
a)	Me	H	H	Me
b)	t-Bu	H	H	Me
c)	t-Bu	Me	H	H
d)	t-Bu	H	Me	H
f)	t-Bu	$-(CH_2)_3-$		H
j)	Me	Me	H	H



(315)

The less soluble products are highly coloured, often virtually black solids, usually possessing a metallic surface sheen which appeared to have a green tinge. These products form small crystals, although the product from the reaction involving carbaldehyde (276d) was obtained as green microprisms, and is currently undergoing a structure determination by X-ray crystallography. These compounds are relatively unstable to light, especially whilst in solution during the work-up, and so proved difficult to purify. Notwithstanding this, microanalytical data was obtained that agreed well with calculated values based on structures (315 a-d,f,j).

The compounds melted over a range of between 2° and 4°C, and with the exception of the product (315a), between the temperature of 169°C and 189°C. The selone (315a) melted between 121°C and 125°C, and was

obtained in only 3.3.% yield, whereas the other selones were obtained in yields of between 19.2% and 26.8%. The combined yields of the carboselenaldehyde (285) and the selone (315) are in the range 54.2% to 70.2%, with the exception of the reaction involving carbaldehyde (276a), where the combined yield of the two products (285a) and (315a) was only 23.0%.

The mass spectral data of selones (315) (Appendix 3) indicates that although the molecular ion cluster was not observed, the cluster corresponding to (M^+-CH_3) was usually present. Many clusters observed in the spectra were consistent with the expected pattern for two selenium atoms, as shown in Appendix 3. Characteristic clusters were also observed corresponding to the loss of a selenoformyl group, and apparently, to the indolizine-3-carboselenaldehyde structures (285), eg. at m/z = 279 for the 1-methyl-2-t-butyl compound (285c).

The compounds (315) were very insoluble for the purposes of n.m.r. spectroscopy. However, spectra were obtained in deuterated dichloromethane, using a high-field n.m.r. spectrometer. The data are listed in Appendices 1 and 2.

The proton n.m.r. spectra of the selones (315 a-d,f,j) show that the indolizine system has remained intact in these compounds, since the same pattern of signals is observed as for the carboselenaldehydes (285). The only small difference is that the H_5 signals (H_4 in the case of the compound obtained from the carbaldehyde (276f)), which occur between δ 10.12 ppm and 10.55 ppm, are further upfield by approximately 1.75 ppm than the H_5 signals of the carboselenaldehydes (285 a-d,f,j). There is however, no signal in the range observed for the CHSe group in compounds (285 a-d,f,j), namely δ 12.09 ppm to 12.78 ppm. Instead, a signal occurs in the range δ 8.70 ppm to 9.21 ppm.

The signals furthest upfield within this range are obtained from the compounds with a 2-methyl substituent in the indolizine system (δ 8.70 ppm and 8.77 ppm for the compounds proposed as (315 a,j) respectively), and if these values are excluded, then the range reduces to δ 9.01 ppm to 9.21 ppm. This reduction in the size of the range parallels that observed for the tungsten complexes (290), as described in Section 3.C., and is therefore further evidence for the presence of the indolizine system.

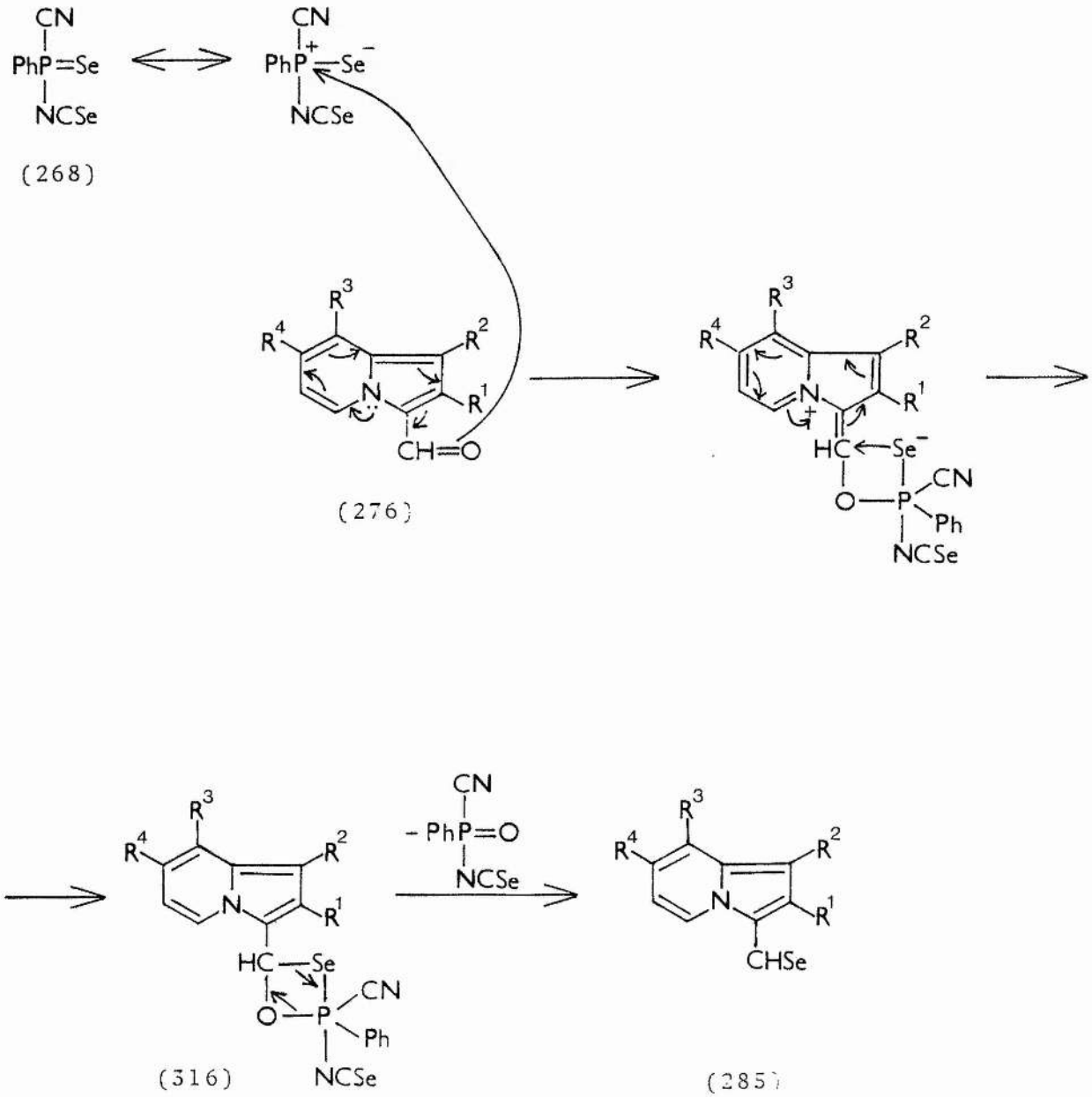
The observation that the indolizine system has remained intact may also be drawn from the carbon-13 n.m.r. spectra. Once again, the relevant signals are comparable with those of the carboselenaldehydes (285 a-d,f,j). The signals corresponding to C_1 (C_{9a} in the case of the proposed compound (315f)) are still the most shielded of all the unsubstituted ring carbon atoms. Those of carbon atom C_3 (C_2 in the case of the compound (315f)) have a different range of chemical shift values, (δ 122.83 ppm to 124.54 ppm), when compared with the corresponding signals in the spectra of carboselenaldehydes (285), (δ 141.98 ppm to 143.78 ppm). This is understandable, since the chemical environment of these carbon atoms has obviously undergone some alteration.

The other fact that is immediately apparent is that there are two additional signals downfield in the carbon-13 n.m.r. spectra, at approximately δ 200 ppm. One occurs between δ 203.52 ppm and 204.36 ppm, and the other between δ194.10 ppm and 195.20 ppm. There is also no signal observed in the range observed for the CHSe group in the compounds (285), δ 176.79 ppm to 182.57 ppm. Instead, a signal is present between δ 146.16 ppm and 149.58 ppm. If only the compounds possessing a 2-t-butyl substituent (315 b-d,f) are considered, then

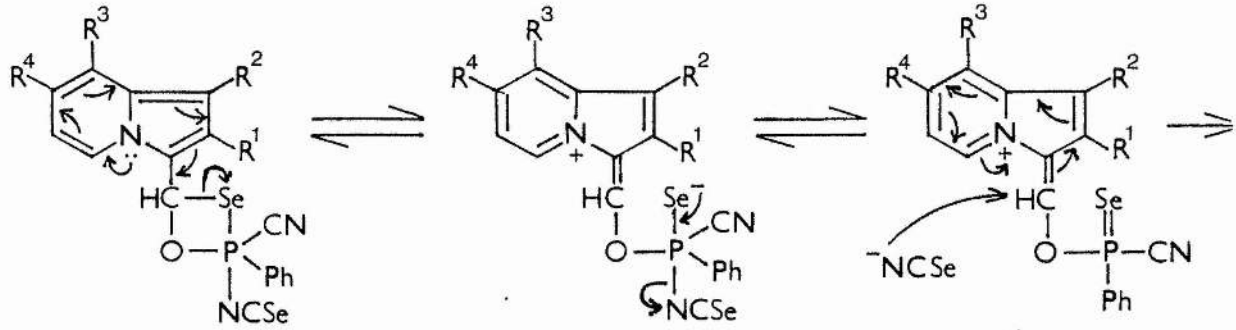
the signals occurs between δ 148.18 ppm and 149.58 ppm.

From the fact that the indolizine system has remained intact, and the fact that the C_3 carbon atom substituent has the empirical formula $C_3HN_2Se_3$, as determined by microanalytical data, these compounds may be formulated as having the structure (315). A mechanism is therefore required that can result in not only the formation of the carbaldehydes (285), but also the structure proposed as (315).

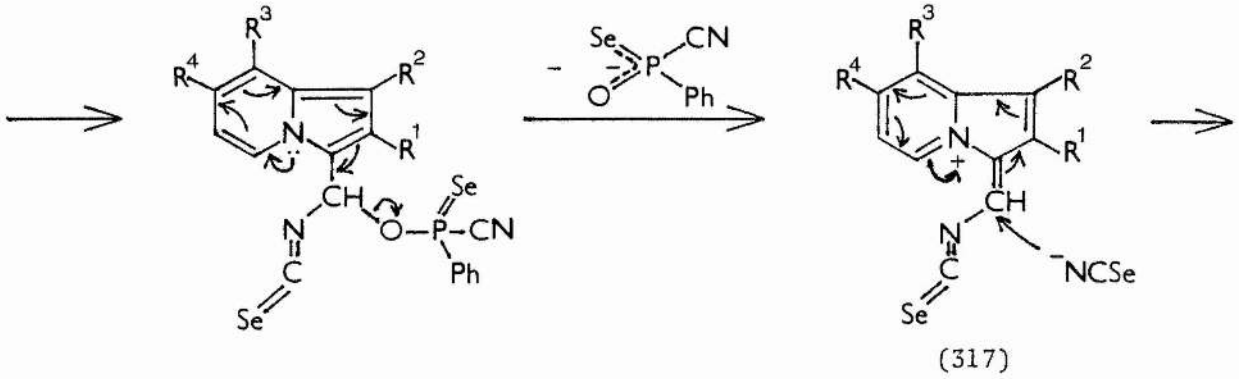
If the carboselenaldehydes (285) are produced by a mechanism analogous to that described in Section 3.B., it may be as follows.



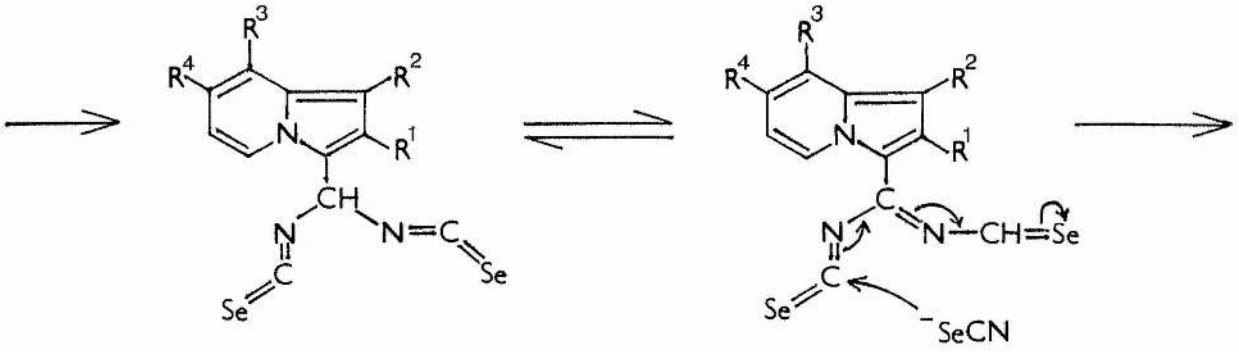
The mechanism accounts for the formation of the carboselenaldehydes (285). If the intermediate (316) was to react slightly differently in addition to the above manner, then the following mechanism for the synthesis of selones (315) may be postulated.

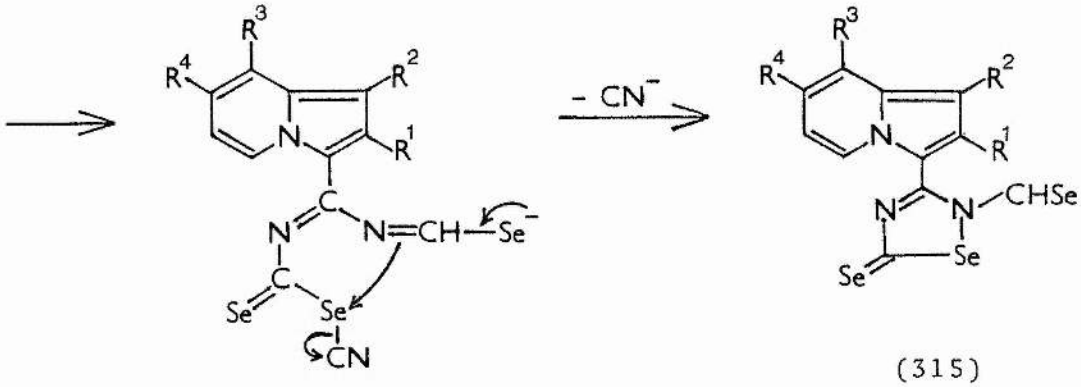


(316)



(317)





(315)

If the selenium anion is able to react as shown, then the selenocyanate anion may be displaced. This ambidentate anion may then attack the "carbaldehyde" carbon atom such that the phosphorus(V) moiety may be displaced as depicted. Additional selenocyanate anions are present, since the original tetramethylammonium selenocyanate reactant (262) was in excess. A second selenocyanate anion may therefore attack the same carbon atom as the first selenocyanate anion. If a proton transfer now occurs, then a selenoformyl function can be obtained. This species may then be attacked by a third selenocyanate anion to form the proposed selone (315).

There is no experimental evidence for this proposed mechanism, but it offers a route whereby compounds with the structure (315) may be formed.

Having now proposed the structure (315) as a possibility for the less soluble compounds obtained in these reactions, it has to be noted that there are several unexpected details in the various analyses, although a structure analysis may prove them to be simply a function of these compounds.

The first concerns the clusters of peaks observed in the mass

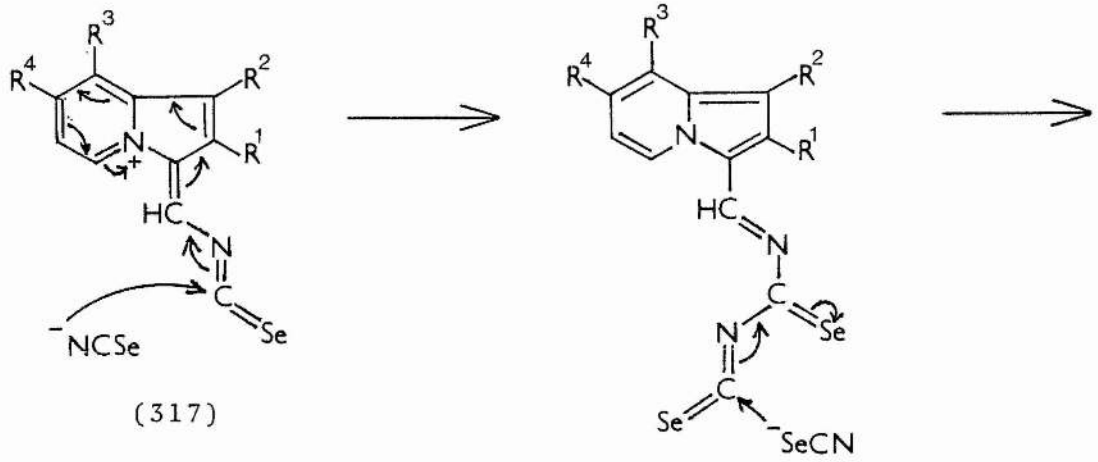
spectra at the mass of the carboselenaldehydes (285). It is difficult to understand how such a moiety may be formed in the mass spectrometer when the selenoformyl group is not directly bonded to the indolizine ring system. In the proton and carbon-13 n.m.r. spectra, it was observed that no signals occurred in the ranges expected from a comparison with the carboselenaldehyde proton and carbon atom signals of compounds (285). Instead, signals were observed in the ranges δ 8.70 ppm to 9.21 ppm and δ 146.16 ppm to 149.58 ppm, respectively. If these signals are to be assigned to the selenoformyl function in the compounds proposed as the selones (315), then they occur much further upfield than previously experienced.

If the assignment of carbon-13 n.m.r. signals is taken further, then the two signals occurring around δ 200 ppm must presumably be assigned to the C_3 and C_5 carbon atoms of the 1,2,4-selenadiazole system. Whilst the C_5 carbon atom might be expected to occur in this region as a result of the presence of the selone substituent, a carbon atom adjacent to the two nitrogen atoms, such as the C_3 carbon atom, would not normally be expected to occur so far downfield. If however, the carbon-13 n.m.r. data for five-membered heterocycles is examined[264], then the following crude estimation may be made.

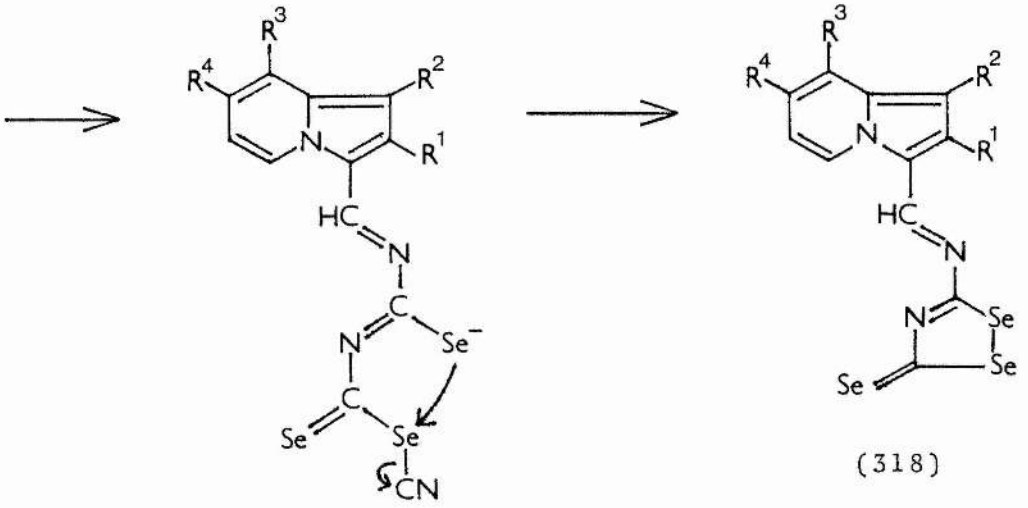
It is known that the effect of introducing a nitrogen atom in position 3 of a pyrrole ring deshields the C_2 carbon atom by approximately 18 ppm. It is also known that introducing a 3-methyl substituent in an isothiazole ring deshields the C_3 carbon atom by approximately 10 ppm, to approximately δ 167 ppm. A rough estimation of the shift of the C_3 carbon atom in 3-methyl-1,2,4-thiadiazole might therefore be approximately δ 185 ppm. Finally, the difference in the shift of the C_3 carbon atom of thiophene and selenophene is approx-

imately 2 ppm. If all these effect are combined to provide a crude estimate of the shift of the C_3 carbon atom of 3-methyl-1,2,4-selenadiazole, then the shift might be of the order of around δ 190 ppm. Obviously, an indolizin-3-yl substituent is not exactly comparable with a methyl substituent, and no allowance has been made for the 2-selenoformyl or 5-selone functions, but the trends might be retained, and so the shift of the C_3 carbon atom in the 1,2,4-selenadiazole ring of the selones (315) might be expected to occur sufficiently far downfield so as to appear in the observed region.

There are therefore certain unexpected observations that may be made from the spectra of these compounds. An alternative mechanism leading to the formation of structure (318) may be considered, involving the attack of a selenocyanate anion on structure (317) at the alternative site shown.



(317)



(318)

This alternative structure may also account for the spectral data obtained. The indolizine ring system has remained intact and so might account for the upfield signals in the proton and carbon-13 n.m.r. spectra. In addition, the signals observed in the range δ 8.70 ppm to 9.21 ppm in the proton n.m.r. spectra, and those in the range δ 146.16 ppm to 149.58 ppm in the carbon-13 n.m.r. spectra, might be accounted for by the CH group adjacent to the C_3 carbon atom in the indolizine ring. Further, the two downfield signals in the carbon-13 n.m.r. spectra may be assigned to the two carbon atoms in the diselenazole ring.

It is therefore possible that the alternative structure (318) may be the correct structure of the relatively insoluble compounds prepared by the reaction of indolizine-3-carbaldehydes (276) with the reagent formed by the reaction of phenyldichlorophosphine (259) with tetramethylammonium selenocyanate (262). It may be noted that this diselenazole ring is an analogue of xanthane hydride[272].

However, the correct structure of this apparently novel system of compounds, which has been prepared under relatively mild conditions,

will only be conclusively determined once the results of a structure analysis are known.

PART C

EXPERIMENTAL

INTRODUCTORY NOTES

Melting points were determined on a Kofler hot-stage apparatus.

Yields refer to recrystallised t.l.c. pure material, unless otherwise stated.

^{1}H n.m.r. spectra were recorded by Mrs.M.H.Smith, Department of Chemistry, University of St. Andrews, using a Bruker WP80 spectrometer operating at 80.024 MHz and at ca. 35°C. ^{1}H n.m.r. spectra were also recorded by Dr.I.H.Sadler and Dr.D.Reed, Department of Chemistry, University of Edinburgh, using a Bruker WH360 spectrometer operating at 360.130 MHz and at ca. 25°C. Solutions in trichloromethane-d, dichloromethane-d_2 and dimethyl sulphoxide-d_6 were 0.4M, except where this concentration could not be obtained, when saturated solutions were employed. Chemical shifts (δ) are expressed in p.p.m. downfield from tetramethylsilane as internal reference, and J values are given in Hz. Unless otherwise stated (d=doublet, t=triplet, qt=quartet, qn=quintet, dd=double doublet, m=multiplet, br=broad), chemical shift values refer to singlet absorptions.

^{13}C n.m.r. spectra were recorded by Mrs.M.H.Smith, Department of Chemistry, University of St. Andrews, using a Varian CFT20 spectrometer operating at 20.000 MHz and at ca. 38°C. ^{13}C n.m.r. spectra were also recorded by Dr.I.H.Sadler and Dr.D.Reed, Department of Chemistry, University of Edinburgh, using a Bruker WH360 spectrometer operating at 90.560 MHz and at ca. 30°C. Solutions in trichloromethane-d, dichloromethane-d_2 and dimethyl sulphoxide-d_6 were 2.0M, except when this concentration could not be obtained, when saturated solutions were employed. Chemical shifts (δ) are expressed in p.p.m.

downfield from tetramethylsilane as internal reference, and J values are given in Hz. Unless otherwise stated (d=doublet, t=triplet, qt=quartet, qn=quintet, dd=double doublet, m=multiplet, br=broad), chemical shift values refer to singlet absorptions.

Mass spectra were recorded, and accurate mass determinations carried out, by Mr.C.Millar, Department of Chemistry, University of St. Andrews, using an AEI MS902 spectrometer.

Carbon, hydrogen and nitrogen elemental microanalyses were determined by Mrs.S.Smith and Miss.C.E.R.Jack, Department of Chemistry, University of St. Andrews, using a Carlo Erba Strumentazione Elemental Analyzer (MOD. 1106). Selenium analyses were carried out by Hr.G.Reuter, Analytische Laboratorien, 5270 Gummersbach, 1 Elbach, Germany.

Procedures

Criteria used in the identification of products included melting points (m.pt.), boiling points (b.pt.), t.l.c. behaviour and n.m.r. and mass spectral data.

Thin layer chromatography (t.l.c.) was carried out on silica (MN Kieselgel-G) coated plates (ca. 0.25mm thick).

Column chromatography was carried out using alumina (Camag 100-250 mesh, activity II, pH 9.3-9.7) and silica (Sorbsil M60 Silica Gel).

Solutions were either dried over anhydrous magnesium sulphate unless otherwise stated.

Solvents were evaporated at reduced pressure using a Buchi rotary film evaporator.

Solids were dried *in vacuo* over phosphorus(V) oxide.

Reactions and subsequent work-ups took place under reduced-light conditions.

Materials

"Ether" refers to diethyl ether. "40-60 Petrol" refers to petroleum ether of boiling range 40- 60°C, and "60-80 petrol" refers to petroleum ether of boiling range 60-80°C.

AR Acetic acid, acetic anhydride, acetone, butan-1-ol, cyclohexane, ethanol, n-hexane, methanol, 40-60 petrol, 60-80 petrol and propan-2-ol were all distilled commercial solvents.

Benzene, toluene and xylene were heated at reflux over sodium wire for one hour, and then distilled to give the dry solvents. Ether was dried over calcium chloride for 48 hours, filtered, heated at reflux over sodium wire for one hour and then distilled. These solvents were stored over sodium wire.

Benzene for chromatography was dried by azeotropic distillation, the first 25% of the distillate being used for extractions when appropriate. Ether for chromatography was dried over calcium chloride for 48 hours, filtered and distilled.

1,2-Dichloroethane, dichloromethane and trichloromethane were heated at reflux over phosphorus(V) oxide for one hour, distilled and redistilled.

Acetonitrile was heated at reflux over calcium hydride (40 mesh/ 95%+, 2g per litre) for one hour and distilled. The distillate was heated at reflux over sodium hydride (80% dispersion in oil, 2g per litre) for one hour and distilled. The distillate was heated at

reflux over phosphorus(V) oxide for one hour and distilled. The distillate was heated at reflux over calcium hydride (40 mesh/95%+, 2g per litre) for one hour and distilled.

N,N-Dimethylformamide was allowed to stand over calcium hydride (40 mesh/95%+, 2g per litre) for one week, then distilled at reduced pressure.

Potassium selenocyanate was fused by heating.

Tetramethylammonium chloride was crushed and oven-dried.

2,6-Dimethyl-4H-pyran-4-one, hexahydro-2H-azepin-2-one and 4-hydroxypyridine were recrystallised commercial reagents.

Bromoacetone, 1-bromo-3,3-dimethylbutan-2-one, 2,4,6-cycloheptatrien-1-one, dichlorophenylphosphine, 6,7-dihydro-5H-1-pyrindine, 2,3-dimethylpyridine, 2,4-dimethylpyridine, 2-ethylpyridine, 1-methylpyrrolidin-2-one, oxalyl chloride, phosphoryl chloride, 6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridine, and 5,6,7,8-tetrahydroquinoline were all distilled commercial reagents.

Mercury(II) acetate, phosphorus(V) sulphide, selenium powder, tetraethylammonium iodide and tungsten hexacarbonyl were all commercial reagents.

N,N-Dimethylthioformamide was prepared from N,N-dimethylformamide[265], as modified by Pettit and Garson[266].

2-(5-t-Butyl-3H-1,2-dithiol-3-ylidene)ethanal was prepared from 5-t-butyl-3-(2-dimethylaminovinyl)-1,2-dithiolylium perchlorate[223], itself prepared from 3-t-butyl-5-methyl-1,2-dithiolylium perchlorate[220]. 3-t-Butyl-5-methyl-1,2-dithiolylium perchlorate had been previously prepared from 5,5-dimethylhexan-2,4-dione[220], and was generously made available for use as a reagent.

2-(5-Phenyl-3H-1,2-dithiol-3-ylidene)ethanal was prepared from

3-(2-dimethylaminovinyl)-5-phenyl-1,2-dithiolylium perchlorate[75], itself prepared from 3-methyl-5-phenyl-1,2-dithiolylium perchlorate[75]. 3-Methyl-5-phenyl-1,2-dithiolylium perchlorate had been previously prepared from 1-phenylbutan-1,3-dione[75], and was generously made available for use as a reagent.

5,6-Dihydro-4H-1,2-benzodithiole-7-carbaldehyde was prepared from 7-(dimethylaminomethylidene)-4,5,6,7-tetrahydro-1,2-benzodithiolylium perchlorate[207], itself prepared from 4,5,6,7-tetrahydro-1,2-benzodithiolylium perchlorate[254]. 4,5,6,7-Tetrahydro-1,2-benzodithiolylium perchlorate had been previously prepared from 2-hydroxymethylenecyclohexanone[207], and was generously made available for use as a reagent.

2-(5-Phenyl-3H-1,2-dithiol-3-ylidene)propanal was prepared from 3-(2-dimethylamino-1-methylvinyl)-5-phenyl-1,2-dithiolylium perchlorate[75], itself prepared from 3-ethyl-5-phenyl-1,2-dithiolylium perchlorate[254]. 3-Ethyl-5-phenyl-1,2-dithiolylium perchlorate had been previously prepared from 1-phenylpentan-1,3-dione[75], and was generously made available for use as a reagent.

5-Phenyl-1,2-dithiol-3-one had previously been prepared according to established methods[267], and was generously made available for use as a reagent.

5-Phenyl-1,2-dithiole-3-thione[267], 5-t-butyl-1,2-dithiole-3-thione[223], 4,5,6,7-tetrahydro-1,2-benzodithiole-3-thione[268] and 4,5-dimethyl-1,2-dithiole-3-thione[269] had previously been prepared according to established methods and were generously made available for the preparation of n.m.r. samples.

Tetraethylammonium pentacarbonyliodotungstate(0) was prepared from tungsten hexacarbonyl and tetraethylammonium iodide[270], as modified by Pogorzelec[258].

2,7-Dimethylindolizine-3-carbaldehyde was prepared from 2,7-dimethylindolizine[249], itself prepared from 1-acetonyl-2,4-dimethylpyridinium bromide[255]. This in turn was prepared from 2,4-dimethylpyridine and bromoacetone[255].

1,2-Dimethylindolizine-3-carboselenaldehyde[74], 1,2-dimethylindolizine-3-carbothialdehyde[248], and 1,2-dimethylindolizine-3-carbaldehyde[248] had been previously prepared from 1,2-dimethylindolizine, and were generously made available for the preparation of n.m.r. samples. 1,2-Dimethylindolizine-3-carbaldehyde was also made available for use as a reagent. 1,2-Dimethylindolizine had been previously prepared from 1-acetonyl-2-ethylpyridinium bromide[255], itself prepared from 2-ethylpyridine and bromoacetone[255].

2-t-Butyl-7-methylindolizine was prepared from 1-(3,3-dimethyl-2-oxobutyl)-2,4-dimethylpyridinium bromide[74], itself prepared from 2,4-dimethylpyridine and 1-bromo-3,3-dimethylbutan-2-one[74].

2-t-Butyl-1-methylindolizine-3-carbothialdehyde had been previously prepared from 2-t-butyl-1-methylindolizine[249], and was generously made available for the preparation of n.m.r. samples. 2-t-Butyl-1-methylindolizine was prepared from 1-(3,3-dimethyl-2-oxobutyl)-2-ethylpyridinium bromide[74], itself prepared from 2-ethylpyridine and 1-bromo-3,3-dimethylbutan-2-one[74].

2-Methylindolizine-3-carbaldehyde had been previously prepared from 2-methylindolizine[248], and was generously made available for the preparation of n.m.r. samples. 2-Methylindolizine had been previously prepared from 1-acetonyl-2-methylpyridinium bromide[255], itself prepared from 2-methylpyridine and bromoacetone[255].

2,8-Dimethylindolizine-3-carbaldehyde had been previously prepared from 2,8-dimethylindolizine[250], and was generously made avail-

able for the preparation of n.m.r. samples. 2,8-Dimethylindolizine had been previously prepared from 1-acetonyl-2,3-dimethylpyridinium bromide[271], itself prepared from 2,3-dimethylpyridine and bromoacetone[271].

2,6-Dimethylindolizine-3-carbaldehyde had been previously prepared from 2,6-dimethylindolizine[250], and was generously made available for the preparation of n.m.r. samples. 2,6-Dimethylindolizine had been previously prepared from 1-acetonyl-2,5-dimethylpyridinium bromide[271], itself prepared from 2,5-dimethylpyridine and bromoacetone[271].

2-t-Butylindolizine-3-carbaldehyde had been previously prepared from 2-t-butylindolizine[250], and was generously made available for the preparation of n.m.r samples. 2-t-Butylindolizine had been previously prepared from 1-(3,3-dimethyl-2-oxobutyl)-2-methylpyridinium bromide[248], itself prepared from 2-methylpyridine and 1-bromo-3,3-dimethylbutan-2-one[248].

Tables of n.m.r. (^{1}H and ^{13}C) and mass spectral data are to be found at the end of the Experimental Section in Appendices 1 - 3 respectively.

1. Synthesis Of Selenium-Transfer Reagents

A. Synthesis of Phenylphosphonoselenoic Dichloride (258)

Red selenium (9.4752g, 120mmol), previously dried over phosphorus(V) oxide for 48 hours, was added in two approximately equal portions to dichlorophenylphosphine (259) (13.20ml, 100mmol) under argon. After each addition of selenium powder, the reaction mixture was heated to 170°-175°C, with swirling. When the first quantity of selenium had completely reacted, the reaction mixture was cooled before the addition of the second portion. When this was added, and after the reaction mixture had been heated with swirling for 20 minutes and no more selenium would react, the reaction mixture was cooled to ambient temperature.

Xylene (25ml) was added to the reaction mixture, the solution was filtered through a pre-weighed sinter and the apparatus washed with xylene (2 x 5ml). The solution was then made up to 50ml, giving a stock solution of phenylphosphonoselenoic dichloride (258) which was approximately 2M in xylene.

The residue in the sinter was washed thoroughly with benzene before it was dried in the oven (80°C). The sinter was then cooled and weighed. The selenium residue (1.6057g, 20.33mmol) indicated that 99.67mmol of selenium had reacted with the dichlorophenylphosphine (259) (100mmol).

$C_6H_5Cl_2PSe$ MW = 257.94(53)

The reaction was repeated as above, except that the solvent benzene was used instead of xylene. Phenylphosphonoselenoic di-

chloride (258) was thus also prepared as an approximately 2M solution in benzene.

B. Synthesis Of Diphenylphosphonoselenoic Chloride (260)

Red selenium (9.4752g, 120mmol), previously dried over phosphorus(V) oxide for 48 hours, was added in two approximately equal portions to chlorodiphenylphosphine (261) (17.95ml, 100mmol) under argon. After each addition of selenium powder, the reaction mixture was heated to 180°-185°C, with swirling. After 20 minutes, and when most of the first quantity of selenium powder had reacted, the reaction mixture was cooled before the addition of the second portion. When this was added, the reaction mixture was heated for 30 minutes until no more selenium powder would react, and was then cooled to ambient temperature.

Xylene (25ml) was added to the reaction mixture, the solution was filtered through a pre-weighed sinter and the apparatus washed with xylene (2 x 5ml). The solution was then made up to 50ml, and should have given a stock solution of diphenylphosphonoselenoic chloride (260) which was approximately 2M in xylene.

The residue in the sinter was washed thoroughly with benzene before it was dried in the oven (80°C). The sinter was then cooled and weighed. The selenium residue (4.1602g, 52.69mmol) indicated that only 67.31mmol of selenium had reacted with the chlorodiphenylphosphine (261) (100mmol).

$C_{12}H_{10}ClP$ MW = 220.6378

$C_{12}H_{10}ClPSe$ MW = 299.59(78)

The fact that the actual product obtained was a mixture of the unreacted chlorodiphenylphosphine (261) and the desired diphenylphosphonoselenoic chloride (260), meant that the preparation of diphenylphosphonoselenoic chloride (260) was not pursued any further.

C. Synthesis Of Tetramethylammonium Selenocyanate (262)

Tetramethylammonium chloride (264) (43.8395g, 400mmol) was added to a solution of potassium selenocyanate (263) (57.6303g, 400mmol) in acetonitrile (1200ml). The solution was heated vigorously at reflux, with stirring, for 4 hours. The resulting white solid was filtered from the hot solution, and the filtrate evaporated to approximately 400ml in volume. The hot solution was filtered once more and then cooled to ambient temperature. The resulting precipitate was filtered, washed with ether and dried in vacuo to afford tetramethylammonium selenocyanate (262), white flakes (24.4111g, 34.1%), decomposition from 251°C. The filtrate was evaporated to approximately 200ml in volume, and a crop of white microprisms (24.0095g, 33.5%) obtained in an identical manner. Further evaporation and filtration afforded white microprisms (10.6079g, 14.8%). The total yield was thus (59.0285g, 82.4%).

$C_5H_{12}N_2Se$ MW = 179.12(32)

Microanalysis	Found:	33.45 %C	6.76 %H	15.70 %N
$C_5H_{12}N_2Se$	Requires:	33.53 %C	6.75 %H	15.64 %N

Accurate mass at $m^{+\cdot}$ 180 Found: No $m^{+\cdot}$ peak was present.

$C_5H_{12}N_2Se$ Requires: 180.0166

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

2. Preparation Of Carbonyl Compounds

A. Preparation Of (1,2-Dithiol-3-ylidene)carbaldehydes (273)

These compounds were prepared as described in the Introductory Notes to the Experimental Section.

B. Preparation Of Indolizine-3-carbaldehydes (276)

1) Preparation Of Pyridinium Bromide Salts (277)

1-(3,3-Dimethyl-2-oxobutyl)-2,3-dimethylpyridinium Bromide (277d)

1-Bromo-3,3-dimethylbutan-2-one (279 : R^1=Bu^t) (13.5ml, 100mmol) was added to 2,3-dimethylpyridine (278d) (11.5ml, 100mmol) in acetone (50ml), and the solution heated at reflux for 1.5 hours. The solution was cooled to ambient temperature and ether added until no further precipitation took place. The precipitate was filtered, washed thoroughly with ether and dried *in vacuo*. 1-(3,3-Dimethyl-2-oxobutyl)-2,3-dimethylpyridinium bromide (277d), cream-coloured microprisms (12.1978g, 42.6%), was afforded from propan-2-ol, m.pt. 214°-216°C.

$C_{13}H_{20}NOBr$ MW = 286.211(1)

Microanalysis	Found:	54.40 %C	7.09 %H	4.82 %N
$C_{13}H_{20}NOBr$	Requires:	54.55 %C	7.04 %H	4.89 %N

Accurate mass at $m^{+\cdot}$ 285 Found: No $m^{+\cdot}$ peak was present.

$C_{13}H_{20}NOBr$ Requires: 285.0728

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

The reaction was repeated under the conditions given below.

1-Bromo-3,3-dimethylbutan-2-one (279 : $R^{1}=Bu^{t}$) (13.5ml, 100mmol) was added to 2,3-dimethylpyridine (278d) (11.5ml, 100mmol) in acetone (20ml) and the solution heated at reflux for 30 minutes.

An identical work-up afforded 1-(3,3-dimethyl-2-oxobutyl)-2,3-dimethylpyridinium bromide (277d), cream-coloured microprisms (14.1417g, 49.4%), from propan-2-ol.

1-(3,3-Dimethyl-2-oxobutyl)-6,7-dihydro-5H-1-pyrindinium Bromide (277e)

1-Bromo-3,3-dimethylbutan-2-one (279 : $R^{1}=Bu^{t}$) (13.5ml, 100mmol) was added to 6,7-dihydro-5H-1-pyrindine (278e) (11.7ml, 100mmol) in acetone (50ml), and the solution heated at reflux for 2 hours. The solution was cooled to ambient temperature and ether added until no further precipitation took place. The precipitate was filtered, washed thoroughly with ether and dried *in vacuo*. 1-(3,3-Dimethyl-2-oxobutyl)-6,7-dihydro-5H-1-pyrindinium bromide (277e), pale purple micro prisms (26.6101g, 89.2%), was afforded from propan-2-ol, m.pt. 205°- 207°C.

$C_{14}H_{20}NOBr$ MW = 298.222(1)

Microanalysis	Found:	56.55 %C	6.89 %H	4.70 %N
$C_{14}H_{20}NOBr$	Requires:	56.39 %C	6.76 %H	4.70 %N

Accurate mass at $m^{+\cdot}$ 297	Found:	No $m^{+\cdot}$ peak was present.
$C_{14}H_{20}NOBr$	Requires:	297.0728

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

1-(3,3-Dimethyl-2-oxobutyl)-5,6,7,8-tetrahydroquinolinium Bromide (277f)

1-Bromo-3,3-dimethylbutan-2-one (279 : $R^{1}=Bu^{t}$) (13.5ml, 100mmol) was added to 5,6,7,8-tetrahydroquinoline (278f) (13.0ml, 100mmol) in acetone (50ml), and the solution heated at reflux for 2 hours. The solution was cooled to ambient temperature and ether added until no further precipitation took place. The precipitate was filtered, washed thoroughly with ether and dried *in vacuo*. 1-(3,3-Dimethyl-2-oxobutyl)-5,6,7,8-tetrahydroquinolinium bromide (277f), cream-coloured microprisms (22.2384g, 71.2%), was afforded from propan-2-ol, m.pt. 186°-188°C.

$C_{15}H_{22}NOBr$ MW = 312.248(9)

Microanalysis	Found:	57.57 %C	7.11 %H	4.42 %N
$C_{15}H_{22}NOBr$	Requires:	57.70 %C	7.10 %H	4.49 %N

Accurate mass at $m^{+\cdot}$ 311	Found:	No $m^{+\cdot}$ peak was present.
$C_{15}H_{22}NOBr$	Requires:	311.0885

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

1-(3,3-Dimethyl-2-oxobutyl)-6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridinium Bromide (277g)

1-Bromo-3,3-dimethylbutan-2-one (279 : $R^1=Bu^t$) (13.5ml, 100mmol) was added to 6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridine (278g) (15.63ml, 100mmol) in acetone (50ml), and the solution heated at reflux for 2 hours. The solution was cooled to ambient temperature and ether added until no further precipitation took place. The precipitate was filtered, washed thoroughly with ether and dried *in vacuo*. 1-(3,3-Dimethyl-2-oxobutyl)-6,7,8,9-tetrahydro-5H-cyclohepta-[b]pyridinium bromide (277g), cream-coloured microprisms (24.3733g, 74.7%), was afforded from propan-2-ol, m.pt. 173.5°-175.5°C.

$C_{16}H_{24}NOBr$ MW = 326.275(7)

Microanalysis	Found:	59.06 %C	7.44 %H	4.21 %N
$C_{16}H_{24}NOBr$	Requires:	58.90 %C	7.41 %H	4.29 %N

Accurate mass at $m^{+\cdot}$ 325 Found: No $m^{+\cdot}$ peak was present.

$C_{16}H_{24}NOBr$ Requires: 325.1041

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

2) Preparation Of Indolizines (280)

2-t-Butyl-8-methylindolizine (280d)

1-(3,3-Dimethyl-2-oxobutyl)-2,3-dimethylpyridinium bromide (277d) (28.6211g, 100mmol) was dissolved in water (300ml) and washed with ether (3 x 300ml). Sodium hydrogen carbonate (33.3g) was added to the aqueous solution, and the solution steam-distilled until it became apparent that no more yellow oil, which was carried over in the distillate, would be carried over. The distillate was extracted with ether (3 x 200ml) and the combined extracts were washed with water (2 x 600ml). The ethereal solution was dried and evaporated, and the residue distilled under reduced pressure (b.pt. 108°C at 0.4mbar pressure), to afford 2-t-butyl-8-methylindolizine (280d) (17.1238g, 91.4%) as a yellow oil.

$C_{13}H_{17}N$ MW = 187.284(0)

Microanalysis	Found:	83.38 %C	9.14 %H	7.47 %N
$C_{13}H_{17}N$	Requires:	83.37 %C	9.15 %H	7.48 %N

Accurate mass at $m^{+\cdot}$ 187 Found: 187.1363

$C_{13}H_{17}N$ Requires: 187.1361

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

1-t-Butyl-7,8-dihydrocyclopent[hi]indolizine (280e)

1-(3,3-Dimethyl-2-oxobutyl)-6,7-dihydro-5H-1-pyrindinium bromide (277e) (29.8222g, 100mmol) was dissolved in water (300ml) and washed with ether (3 x 300ml). Sodium hydrogen carbonate (33.3g) was added to the aqueous solution, and the solution steam-distilled until it became apparent that no product was being carried over in the distillate. The distillate was extracted with ether (3 x 200ml) and the combined extracts were washed with water (2 x 600ml). The ethereal solution was dried and evaporated, but afforded no discernable product.

1-t-Butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]quinoline (280f)

1-(3,3-Dimethyl-2-oxobutyl)-5,6,7,8-tetrahydroquinolinium bromide (277f) (31.2249g, 100mmol) was dissolved in water (300ml) and washed with ether (3 x 300ml). Sodium hydrogen carbonate (33.3g) was added to the aqueous solution, and the solution steam-distilled until it became apparent that no more yellow oil, which was carried over in the distillate, would be carried over. The distillate was extracted with ether (3 x 200ml) and the combined extracts were washed with water

(2 x 600ml). The ethereal solution was dried and evaporated, and the residue distilled under reduced pressure (b.pt. 132°C at 0.8mbar pressure). The yellow distillate, 1-t-butyl-8,9-dihydro-7H-pyrrolo-[3,2,1-ij]quinoline (280f) (13.0766g, 61.3%), crystallised very slowly to give cream-coloured microprisms, m.pt. 42°-45°C.

$C_{15}H_{19}N$ MW = 213.321(8)

Microanalysis	Found:	84.53 %C	9.07 %H	6.55 %N
$C_{15}H_{19}N$	Requires:	84.46 %C	8.98 %H	6.57 %N

Accurate mass at $m^{+\cdot}$ 213	Found:	213.1527
$C_{15}H_{19}N$	Requires:	213.1517

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

1-t-Butyl-7,8,9,10-tetrahydrocyclohept[hi]indolizine (280g)

1-(3,3-Dimethyl-2-oxobutyl)-6,7,8,9-tetrahydro-5H-cyclohepta[b]-pyridinium bromide (277g) (16.3138g, 50mmol) was dissolved in water (200ml) and washed with ether (3 x 200ml). Sodium hydrogen carbonate (16.65g) was added to the aqueous solution, and the solution steam-distilled with super-heated steam until it became apparent that no more yellow oil, which was carried over in the distillate, would be carried over. The distillate was extracted with ether (3 x 200ml) and the combined extracts were washed with water (2 x 600ml). The

ethereal solution was dried and evaporated, and the residue distilled under reduced pressure (b.pt. 148°C at 1.0mbar pressure). The brown distillate, 1-t-butyl-7,8,9,10-tetrahydrocyclohept[hi]indolizine (280g) (9.2743g, 81.6%), crystallised very slowly to give yellow microprisms, m.pt. 35°-39°C.

$C_{16}H_{21}N$ MW = 227.348(6)

Microanalysis	Found:	84.67 %C	9.43 %H	6.09 %N
$C_{16}H_{21}N$	Requires:	84.53 %C	9.31 %H	6.16 %N

Accurate mass at $m^{+\cdot}$ 227	Found:	227.1667
$C_{16}H_{21}N$	Requires:	227.1674

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

3) Preparation Of Indolizine-3-carbaldehydes (276)

2-t-Butyl-7-methylindolizine-3-carbaldehyde (276b)

A solution of phosphoryl chloride (5ml, 55mmol) in N,N-dimethylformamide (50ml) was added dropwise over 30 minutes to a stirred solution of 2-t-butyl-7-methylindolizine (280b) (9.3642g, 50mmol) in N,N-dimethylformamide (50ml) at ambient temperature. The solution was stirred for a further 2 hours, and then aqueous sodium hydroxide solution (250ml of 2M) was added. The solution was cooled to ambient

temperature and benzene (200ml) added. The solution was added to water (500ml) and extracted with benzene (2 x 400ml). The combined benzene extracts were then washed with water (6 x 500ml). The solution was then dried, evaporated and the residue sublimed at reduced pressure. The sublimate afforded 2-t-butyl-7-methylindolizine-3-carbaldehyde (276b), very pale green spars (8.8817g, 82.5%) from n-hexane, m.pt. 72°-75°C. A second crop afforded very pale green microspars (0.4261g, 4.0%) from n-hexane. The total yield was thus (9.3078g, 86.5%).

$C_{14}H_{17}NO$ MW = 215.294(4)

Microanalysis	Found:	78.43 %C	8.15 %H	6.46 %N
$C_{14}H_{17}NO$	Requires:	78.10 %C	7.96 %H	6.51 %N

Accurate mass at $m^{+\cdot}$ 215	Found:	215.1313
$C_{14}H_{17}NO$	Requires:	215.1310

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

2-t-Butyl-1-methylindolizine-3-carbaldehyde (276c)

A solution of phosphoryl chloride (5ml, 55mmol) in N,N-dimethylformamide (50ml) was added dropwise over 30 minutes to a stirred solution of 2-t-butyl-1-methylindolizine (280c) (9.3642g, 50mmol) in N,N-dimethylformamide (50ml) at ambient temperature. The solution was

stirred for a further 2 hours, and then aqueous sodium hydroxide solution (250ml of 2M) was added. The solution was cooled to ambient temperature and benzene (200ml) added. The solution was added to water (500ml) and extracted with benzene (2 x 400ml). The combined benzene extracts were then washed with water (6 x 500ml). The solution was then dried, evaporated and the residue sublimed at reduced pressure. The sublimate afforded 2-t-butyl-1-methylindolizine-3-carbaldehyde (276c), yellow spars (9.8162g, 91.2%) from n-hexane, m.pt. 88°-90°C. A second crop afforded yellow microspars (0.2837g, 2.6%) from n-hexane. The total yield was thus (10.0999g, 93.8%).

$C_{14}H_{17}NO$ MW = 215.294(4)

Microanalysis	Found:	78.37 %C	8.09 %H	6.48 %N
$C_{14}H_{17}NO$	Requires:	78.10 %C	7.96 %H	6.51 %N

Accurate mass at $m^{+\cdot}$ 215	Found:	215.1305
$C_{14}H_{17}NO$	Requires:	215.1310

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

2-t-Butyl-8-methylindolizine-3-carbaldehyde (276d)

A solution of phosphoryl chloride (5ml, 55mmol) in N,N-dimethylformamide (50ml) was added dropwise over 30 minutes to a stirred solution of 2-t-butyl-8-methylindolizine (280d) (9.3642g, 50mmol) in

N,N-dimethylformamide (50ml) at ambient temperature. The solution was stirred for a further 2 hours, and then aqueous sodium hydroxide solution (250ml of 2M) was added. The solution was cooled to ambient temperature and benzene (200ml) added. The solution was added to water (300ml) and extracted with benzene (2 x 250ml). The combined extracts were then washed with water (6 x 500ml). The solution was then dried, evaporated and the residue chromatographed on alumina (10 x 4.2cm), initially using benzene as eluant, but ultimately benzene/ether (9:1). Yellow eluates were evaporated, and afforded 2-t-butyl-8-methylindolizine-3-carbaldehyde (276d), yellow prisms (10.3016g, 95.7%) from n-hexane, m.pt. 113°-114°C. A second crop afforded yellow prisms (0.0167g, 0.2%) from n-hexane. The total yield was thus (10.3183g, 95.9%).

$C_{14}H_{17}NO$ MW = 215.294(4)

Microanalysis	Found:	78.30 %C	8.12 %H	6.49 %N
$C_{14}H_{17}NO$	Requires:	78.10 %C	7.96 %H	6.51 %N

Accurate mass at $m^{+\cdot}$ 215	Found:	215.1304
$C_{14}H_{17}NO$	Requires:	215.1310

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

1-t-Butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]-quinoline-2-carbaldehyde (276f)

A solution of phosphoryl chloride (5ml, 55mmol) in N,N-dimethylformamide (50ml) was added dropwise over 30 minutes to a stirred solution of 1-t-butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]quinoline (280f) (10.6661g, 50mmol) in N,N-dimethylformamide (50ml) at ambient temperature. The solution was stirred for a further 2 hours, and then aqueous sodium hydroxide solution (250ml of 2M) was added. The solution was cooled to ambient temperature and benzene (200ml) added. The solution was added to water (300ml) and extracted with benzene (2 x 250ml). The combined extracts were then washed with water (6 x 500ml). The solution was then dried, evaporated and the residue chromatographed on alumina (10 x 4.2cm), initially using benzene as eluant, but ultimately benzene/ether (9:1). Yellow eluates were evaporated, and afforded 1-t-butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]-quinoline-2-carbaldehyde (276f), yellow needles (9.6491g, 80.0%) from n-hexane, m.pt. 164°- 166°C. A second crop afforded yellow spars (1.4822g, 12.3%) from n-hexane. The total yield was thus (11.1313g, 92.2%).

$C_{16}H_{19}NO$ MW = 241.332(2)

Microanalysis	Found:	79.67 %C	8.01 %H	5.81 %N
$C_{16}H_{19}NO$	Requires:	79.63 %C	7.94 %H	5.80 %N

Accurate mass at $m^{+\cdot}$ 241	Found:	241.1474
$C_{16}H_{19}NO$	Requires:	241.1467

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

1-t-Butyl-7,8,9,10-tetrahydrocyclohept[hi]-indolizine-2-carbaldehyde (276g)

A solution of phosphoryl chloride (5ml, 55mmol) in N,N-dimethylformamide (50ml) was added dropwise over 30 minutes to a stirred solution of 1-t-butyl-7,8,9,10-tetrahydrocyclohept[hi]indolizine (280g) (11.3674g, 50mmol) in N,N-dimethylformamide (50ml) at ambient temperature. The solution was stirred for a further 2 hours, and then aqueous sodium hydroxide solution (250ml of 2M) was added. The solution was cooled to ambient temperature and benzene (200ml) added. The solution was added to water (300ml) and extracted with benzene (2 x 250ml). The combined extracts were then washed with water (6 x 500ml). The solution was then dried, evaporated and the residue chromatographed on alumina (10 x 4.2cm), initially using benzene as eluant, but ultimately benzene/ether (9:1). Yellow eluates were evaporated, and afforded 1-t-butyl-7,8,9,10-tetrahydrocyclohept[hi]-indolizine-2-carbaldehyde (276g), clusters of pale yellow microprisms (7.4374g, 58.3%) from n-hexane, m.pt. 92°-93°C. A second crop afforded clusters of pale yellow microprisms (0.6248g, 4.9%) from n-hexane. The total yield was thus (8.0622g, 63.1%).

$C_{17}H_{21}NO$ MW = 255.359(0)

Microanalysis	Found:	79.75 %C	8.36 %H	5.39 %N
$C_{17}H_{21}NO$	Requires:	79.96 %C	8.29 %H	5.48 %N

Accurate mass at $m^{+\cdot}$ 255	Found:	255.1629
$C_{17}H_{21}NO$	Requires:	255.1623

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

3. Reactions Involving Selenium-Transfer Reagents

A. Synthesis Of 1,6aλ^4-dithia-6-selenapentalenes (282)

2-Phenyl-1,6aλ^4-dithia-6-selenapentalene (282a)

Phenylphosphonoselenoic dichloride (258) (6.25ml of approx. 2M in xylene, approx. 12.5mmol) was added to 2-(5-phenyl-3H-1,2-dithiol-3-ylidene)ethanal (273a) (1.1016g, 5mmol) in benzene (50ml), and the solution heated at reflux for 15 minutes. The solution was cooled to ambient temperature and benzene (350ml) added. The solution was washed with water (1 x 400ml) and then with aqueous sodium hydroxide (250ml of 0.5M). The solution was then filtered through a bed of Hyflo Super-Cel (1cm). The filtrate was washed with water (2 x 250ml), dried, evaporated and the residue chromatographed on alumina (40 x 2.7cm) using 60-80 petrol/benzene (2:1) as eluant. Purple eluates were evaporated, and afforded 2-phenyl-1,6aλ^4-dithia-6-selenapentalene (282a), purple flakes with a bronze lustre (0.5660g, 40.0%) from cyclohexane, m.pt. 144°-145°C. A second crop afforded purple spars (0.0790g, 5.6%) from n-hexane. The total yield was thus (0.6450g, 45.6%).

$C_{11}H_8S_2Se$ MW = 283.27(22)

Microanalysis	Found:	46.68 %C	2.78 %H
$C_{11}H_8S_2Se$	Requires:	46.64 %C	2.85 %H

Accurate mass at $m^{+\cdot}$ 284 Found: 283.9237

$C_{11}H_8S_2Se$ Requires: 283.9233

^1H nmr - see Appendix 1

Mass spectral data - see Appendix 3

The reaction was repeated under the conditions given below.

Phenylphosphonoselenoic dichloride (258) (5.0ml of approx. 2M in xylene, approx. 10mmol) was added to 2-(5-phenyl-3H-1,2-dithiol-3-ylidene)ethanal (273a) (1.1016g, 5mmol) in benzene (50ml), and the solution heated at reflux for 15 minutes.

An identical work-up afforded 2-phenyl-1,6aλ^4-dithia-6-selena-pentalene (282a), purple flakes with a bronze lustre (0.5340g, 37.7%) from cyclohexane. A second crop afforded purple spars (0.0630g, 4.4%) from n-hexane. The total yield was thus (0.5970g, 42.1%).

The reaction was repeated once more under the conditions given below.

Phenylphosphonoselenoic dichloride (258) (6.25ml of approx. 2M in xylene, approx. 12.5mmol) was added to 2-(5-phenyl-3H-1,2-dithiol-3-ylidene)ethanal (273a) (1.1016g, 5mmol) in dichloromethane (50ml), and the solution heated at reflux for 1.5 hours.

An identical work-up afforded 2-phenyl-1,6aλ^4-dithia-6-selena-pentalene (282a), purple flakes with a bronze lustre (0.6490g, 45.7%) from cyclohexane. A second crop afforded purple spars (0.0680g, 4.8%) from n-hexane. The total yield was thus (0.7170g, 50.5%).

2-t-Butyl-1,6aλ^4-dithia-6-selenapentalene (282b)

Phenylphosphonoselenoic dichloride (258) (6.25ml of approx. 2M in xylene, approx. 12.5mmol) was added to 2-(5-t-butyl-3H-1,2-dithiol-3-ylidene)ethanal (273b) (1.0016g, 5mmol) in benzene (50ml), and the solution heated at reflux for 15 minutes. The solution was cooled to ambient temperature and benzene (350ml) added. The solution was washed with water (1 x 400ml) and then with aqueous sodium hydroxide (250ml of 0.5M). The solution was then filtered through a bed of Hyflo Super-Cel (1cm). The filtrate was washed with water (2 x 250ml), dried, evaporated and the residue chromatographed on alumina (40 x 2.7cm) using 60-80 petrol/benzene (2:1) as eluant. Purple eluates were evaporated, and afforded 2-t-butyl-1,6aλ^4-dithia-6-selenapentalene (282b), purple needles (0.5218g, 39.6%) from methanol, m.pt. 72°-73°C. A second crop afforded purple needles (0.1434g, 10.9%) from methanol. The total yield was thus (0.6652g, 50.5%).

$C_9H_{12}S_2Se$ MW = 263.28(18)

Microanalysis	Found:	40.78 %C	4.62 %H
$C_9H_{12}S_2Se$	Requires:	41.06 %C	4.59 %H

Accurate mass at $m^{+\cdot}$ 264	Found:	263.9535
$C_9H_{12}S_2Se$	Requires:	263.9546

^1H nmr - see Appendix 1

Mass spectral data - see Appendix 3

The reaction was repeated under the conditions given below.

Phenylphosphonoselenoic dichloride (258) (6.25ml of approx. 2M in xylene, approx. 12.5mmol) was added to 2-(5-t-butyl-3H-1,2-dithiol-3-ylidene)ethanal (273b) (1.0016g, 5mmol) in dichloromethane (50ml), and the solution heated at reflux for 1.5 hours.

An identical work-up afforded 2-t-butyl-1,6aλ^4-dithia-6-selenapentalene (282b), purple needles (0.5234g, 39.8%) from methanol. A second crop afforded purple needles (0.1496g, 11.4%) from methanol. The total yield was thus (0.6730g, 51.1%).

2-Phenyl-4-methyl-1,6aλ^4-dithia-6-selenapentalene (282c)

Phenylphosphonoselenoic dichloride (258) (6.25ml of approx. 2M in xylene, appprox. 12.5mmol) was added to 2-(5-phenyl-3H-1,2-dithiol-3-ylidene)propanal (273c) (1.1717g, 5mmol) in benzene (50ml), and the solution heated at reflux for 15 minutes. The solution was cooled to ambient temperature and benzene (350ml) added. The solution was washed with water (1 x 400ml) and then with aqueous sodium hydroxide (250ml of 0.5M). The solution was then filtered through a bed of Hyflo Super-Cel (1cm). The filtrate was washed with water (2 x 250ml), dried, evaporated and the residue chromatographed on alumina (40 x 2.7cm) using 60-80 petrol/benzene (2:1) as eluant. Purple eluates were evaporated, and afforded 2-phenyl-4-methyl-1,6aλ^4-dithia-6-selenapentalene (282c), purple needles (0.9282g, 62.4%) from cyclohexane, m.pt. 118°-119°C. A second crop afforded purple needles (0.1150g, 7.7%) from n-hexane. The total yield was thus (1.0432g, 70.2%).

$C_{12}H_{10}S_2Se$ MW = 297.29(90)

Microanalysis	Found:	48.60 %C	3.33 %H
$C_{12}H_{10}S_2Se$	Requires:	48.48 %C	3.39 %H

Accurate mass at $m^{+\cdot}$ 298	Found:	297.9398
$C_{12}H_{10}S_2Se$	Requires:	297.9389

^1H nmr - see Appendix 1

Mass spectral data - see Appendix 3

The reaction was repeated under the conditions given below.

Phenylphosphonoselenoic dichloride (258) (6.25ml of approx. 2M in xylene, approx. 12.5mmol) was added to 2-(5-phenyl-3H-1,2-dithiol-3-ylidene)propanal (273c) (1.1717g, 5mmol) in dichloromethane (50ml), and the solution heated at reflux for 1.5 hours.

An identical work-up afforded 2-phenyl-4-methyl-1,6aλ^4-dithia-6-selenapentalene (282c), purple needles (0.7601g, 51.1%) from cyclohexane. A second crop afforded purple needles (0.1095g, 7.4%) from n-hexane. The total yield was thus (0.8696g, 58.5%).

4,5-Dihydro-3H-[1,2]thiaselenolo[4,5,1-hi]-[1,2]benzodithiole-7a-S^4 (282d)

Phenylphosphonoselenoic dichloride (258) (6.25ml of approx. 2M in xylene, approx. 12.5mmol) was added to 5,6-dihydro-4H-1,2-benzodithiole-7-carbaldehyde (273d) (0.9214g, 5mmol) in benzene (50ml), and

the solution heated at reflux for 15 minutes. The solution was cooled to ambient temperature and benzene (350ml) added. The solution was washed with water (1 x 400ml) and then with aqueous sodium hydroxide (250ml of 0.5M). The solution was then filtered through a bed of Hyflo Super-Cel (1cm). The filtrate was washed with water (2 x 250ml), dried, evaporated and the residue chromatographed on alumina (40 x 2.7cm) using 60-80 petrol/benzene (2:1) as eluant. Purple eluates were evaporated, and afforded a mixture of 4,5-dihydro-3H-[1,2]thiaselenolo[4,5,1-hi][1,2]benzodithiole-7a-S^4 (282d) and 4,5-dihydro-3H-[1,2]dithiolo[4,5,1-hi][1,2]benzodithiole-7a-S^4 (283d), purple flakes (0.3103g, 25.1%) from n-hexane, m.pt. 79°-80°C. A second crop afforded purple flakes (0.0869g, 7.0%) from n-hexane. The total yield was thus (0.3972g, 32.1%).

$C_8H_8S_2Se$ MW = 247.23(84)

Microanalysis	Found:	40.17 %C	3.38 %H
$C_8H_8S_2Se$	Requires:	38.86 %C	3.26 %H
$C_8H_8S_3$	Requires:	47.96 %C	4.02 %H

Accurate mass at $m^{+\cdot}$ 248	Found:	247.9240
$C_8H_8S_2Se$	Requires:	247.9233

^1H nmr - see Appendix 1

Mass spectral data - see Appendix 3

The reaction was repeated under the conditions given below.

Phenylphosphonoselenoic dichloride (258) (6.25ml of approx. 2M in xylene, approx. 12.5mmol) was added to 5,6-dihydro-4H-1,2-benzodithiole-7-carbaldehyde (273d) (0.9214g, 5mmol) in dichloromethane (50ml), and the solution heated at reflux for 1.5 hours.

An identical work-up afforded a similar mixture of 4,5-dihydro-3H-[1,2]thiaselenolo[4,5,1-hi][1,2]benzodithiole-7a-S^4 (282d) and 4,5-dihydro-3H-[1,2]dithiolo[4,5,1-hi][1,2]benzodithiole-7a-S^4 (283d), purple flakes (0.3640g, 29.5%) from n-hexane. A second crop afforded purple flakes (0.1289g, 10.4%) from n-hexane. The total yield was thus (0.4929g, 39.9%).

It was evident from the mass spectral data, the nmr data and the microanalytical data that the desired product, namely 4,5-dihydro-3H-[1,2]thiaselenolo[4,5,1-hi][1,2]benzodithiole-7a-S^4 (282d), was never isolated from the corresponding dithiolobenzodithiole (283d).

B. Synthesis Of Indolizine-3-carboselenaldehydes (285)

2,7-Dimethylindolizine-3-carboselenaldehyde (285a)

Phenylphosphonoselenoic dichloride (258) (3.75ml of approx. 2M in xylene, approx. 7.5mmol) was added to a stirred solution of 2,7-dimethylindolizine-3-carbaldehyde (276a) (0.8661g, 5mmol) in dichloromethane (100ml). The solution was stirred at ambient temperature for 10 minutes, then dichloromethane (400ml) added. The solution was washed with aqueous sodium hydroxide solution (200ml of 0.5M) and then with water (400ml). The solution was dried and evaporated and then benzene (50ml) added to the residue. This was in turn evaporated and the residue extracted with aliquots of warm benzene (100ml in total). The combined extracts were cooled to ambient temperature and chromatographed without further evaporation on alumina (35 x 2.6cm) using benzene as eluant. Initial yellow eluates were discarded, and the eluant changed to benzene/ether (9:1). Green eluates were evaporated and then dissolved in dichloromethane (10ml). After filtration, the solution was rapidly reduced to approximately 3ml in volume on a water-bath and warm n-hexane (50ml) added. The solution was allowed to crystallise and the precipitate washed once with n-hexane to afford 2,7-dimethylindolizine-3-carboselenaldehyde (285a), green needles (0.3583g, 30.3%), m.pt. 140°-142°C, with slight decomposition from 139°C. A second crop afforded green needles (0.0521g, 4.4%) from n-hexane. The total yield was thus (0.4104g, 34.8%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{11}H_{11}NSe$ MW = 236.17(46)

Microanalysis	Found:	55.83 %C	4.62 %H	5.80 %N
$C_{11}H_{11}NSe$	Requires:	55.94 %C	4.69 %H	5.93 %N

Accurate mass at $m^{+\cdot}$ 237 Found: 237.0053

$C_{11}H_{11}NSe$ Requires: 237.0057

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

2-t-Butyl-7-methylindolizine-3-carboselenaldehyde (285b)

Phenylphosphonoselenoic dichloride (258) (3.75ml of approx. 2M in xylene, approx. 7.5mmol) was added to a stirred solution of 2-t-butyl-7-methylindolizine-3-carbaldehyde (276b) (1.0765g, 5mmol) in dichloromethane (100ml). The solution was stirred at ambient temperature for 10 minutes, then dichloromethane (400ml) added. The solution was washed with aqueous sodium hydroxide solution (200ml of 0.5M) and then with water (400ml). The solution was dried and evaporated and then benzene (50ml) added to the residue. This was in turn evaporated and the residue extracted with aliquots of warm benzene (100ml in total). The combined extracts were cooled to ambient temperature and chromatographed without further evaporation on alumina (35 x 2.6cm) using benzene as eluant. Initial yellow eluates were discarded, and the eluant changed to benzene/ether (9:1). Green eluates were evaporated and then dissolved in dichloromethane (10ml). After filtration, the solution was rapidly reduced to approximately 3ml in volume on the water-bath and warm n-hexane (50ml) added. The solution was allowed

to crystallise and the precipitate washed once with n-hexane to afford 2-t-butyl-7-methylindolizine-3-carboselenaldehyde (285b), purple plates (0.8755g, 62.9%), m.pt. 108°-110°C, with slight decomposition from 106°C. A second crop afforded purple plates (0.1320g, 9.5%) from n-hexane. The total yield was thus (1.0075g, 72.4%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{14}H_{17}NSe$ MW = 278.25(50)

Microanalysis	Found:	60.45 %C	6.10 %H	4.95 %N	28.35 %Se
$C_{14}H_{17}NSe$	Requires:	60.43 %C	6.16 %H	5.03 %N	28.38 %Se

Accurate mass at $m^{+\cdot}$ 279 Found: 279.0534

$C_{14}H_{17}NSe$ Requires: 279.0526

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

2-t-Butyl-1-methylindolizine-3-carboselenaldehyde (285c)

Phenylphosphonoselenoic dichloride (258) (3.75ml of approx. 2M in xylene, approx. 7.5mmol) was added to a stirred solution of 2-t-butyl-1-methylindolizine-3-carbaldehyde (276c) (1.0765g, 5mmol) in dichloromethane (100ml). The solution was stirred at ambient temparature for 10 minutes, then dichloromethane (400ml) added. The solution was washed with aqueous sodium hydroxide solution (200ml of 0.5M) and then

with water (400ml). The solution was dried and evaporated and then benzene (50ml) added to the residue. This was in turn evaporated and the residue extracted with aliquots of warm benzene (100ml in total). The combined extracts were cooled to ambient temperature and chromatographed without further evaporation on alumina (35 x 2.6cm) using benzene as eluant. Initial yellow eluates were collected, and the eluant changed to benzene/ether (9:1). Green eluates were evaporated and then dissolved in dichloromethane (10ml). After filtration, the solution was rapidly reduced to approximately 3ml in volume on a water-bath and warm n-hexane (50ml) added. The solution was allowed to crystallise and the precipitate washed once with n-hexane to afford 2-t-butyl-1-methylindolizine-3-carboselenaldehyde (285c), green needles (0.3790g, 27.2%), m.pt. 167°-169°C, with slight decomposition from 165°C. A second crop afforded green needles (0.0637g, 4.6%) from n-hexane. The total yield was thus (0.4427g, 31.8%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{14}H_{17}NSe$ MW = 278.25(50)

Microanalysis	Found:	60.69 %C	6.27 %H	4.94 %N
$C_{14}H_{17}NSe$	Requires:	60.43 %C	6.16 %H	5.03 %N

Accurate mass at $m^{+\cdot}$ 279	Found:	279.0518
$C_{14}H_{17}NSe$	Requires:	279.0526

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

The initial yellow eluates were evaporated and the residue re-chromatographed on alumina (15 x 2.6cm) using 40-60 petrol/benzene (4:1) as eluant. Yellow eluates were evaporated and afforded 1,2-di-(2-t-butyl-1-methylindolizin-3-yl)ethene (288c), golden oil (0.4625g, 46.4% [w.r.t. the reactant indolizine-3-carbaldehyde (276c)]).

$C_{28}H_{34}N_2$ MW = 398.590(0)

Microanalysis	Found:	84.08 %C	8.56 %H	7.31 %N
$C_{28}H_{34}N_2$	Requires:	84.37 %C	8.60 %H	7.03 %N

Mass spectral data - see Appendix 3

2-t-Butyl-8-methylindolizine-3-carboselenaldehyde (285d)

Phenylphosphonoselenoic dichloride (258) (3.75ml of approx. 2M in xylene, approx. 7.5mmol) was added to a stirred solution of 2-t-butyl-8-methylindolizine-3-carbaldehyde (276d) (1.0765g, 5mmol) in dichloromethane (100ml). The solution was stirred at ambient temperature for 10 minutes, then dichloromethane (400ml) added. The solution was washed with aqueous sodium hydroxide solution (200ml of 0.5M) and then with water (400ml). The solution was dried and evaporated and then benzene (50ml) added to the residue. This was in turn evaporated and the residue extracted with aliquots of warm benzene (100ml in total). The combined extracts were cooled to ambient temperature and chromatographed without further evaporation on alumina (35 x 2.6cm) using

benzene as eluant. Initial yellow eluates were discarded, and the eluant changed to benzene/ether (9:1). Green eluates were evaporated and then dissolved in dichloromethane (10ml). After filtration, the solution was rapidly reduced to approximately 3ml in volume on the water-bath and warm n-hexane (50ml) added. The solution was allowed to crystallise and the precipitate washed once with n-hexane to afford 2-t-butyl-8-methylindolizine-3-carboselenaldehyde (285d), olive microspars (0.7116g, 51.1%), m.pt. 169.5°-170.5°C, with slight decomposition from 168°C. A second crop afforded olive microspars (0.0525g, 3.8%) from n-hexane. The total yield was thus (0.7641g, 54.9%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{14}H_{17}NSe$ MW = 278.25(50)

Microanalysis	Found:	60.75 %C	6.20 %H	5.02 %N
$C_{14}H_{17}NSe$	Requires:	60.43 %C	6.16 %H	5.03 %N

Accurate mass at $m^{+\cdot}$ 279	Found:	279.0534
$C_{14}H_{17}NSe$	Requires:	279.0526

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

1-t-Butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]-quinoline-2-carboselenaldehyde (285f)

Phenylphosphonoselenoic dichloride (258) (3.75ml of approx. 2M in xylene, approx. 7.5mmol) was added to a stirred solution of 1-t-butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]quinoline-2-carbaldehyde (276f) (1.2067g, 5mmol) in dichloromethane (100ml). The solution was stirred at ambient temperature for 10 minutes, then dichloromethane (400ml) added. The solution was washed with aqueous sodium hydroxide solution (200ml of 0.5M) and then with water (400ml). The solution was dried and evaporated and then benzene (50ml) added to the residue. This was in turn evaporated and the residue extracted with aliquots of warm benzene (100ml in total). The combined extracts were cooled to ambient temperature and chromatographed without further evaporation on alumina (35 x 2.6cm) using benzene as eluant. Initial yellow eluates were discarded, and the eluant changed to benzene/ether (9:1). Green eluates were evaporated and then dissolved in dichloromethane (10ml). After filtration, the solution was rapidly reduced to approximately 3ml in volume on a water-bath and warm n-hexane (50ml) added. The solution was allowed to crystallise and the precipitate washed once with n-hexane to afford 1-t-butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]-quinoline-2-carboselenaldehyde (285f), green microneedles (0.7935g, 52.2%), m.pt. 186.5°-188°C, with slight decomposition from 184°C. A second crop afforded green microneedles (0.0428g, 2.8%) from n-hexane. The total yield was thus (0.8363g, 55.0%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{16}H_{19}NSe$ MW = 304.29(28)

Microanalysis	Found:	63.11 %C	6.33 %H	4.62 %N	26.15 %Se
$C_{16}H_{19}NSe$	Requires:	63.15 %C	6.29 %H	4.60 %N	25.95 %Se

Accurate mass at $m^{+\cdot}$ 305 Found: 305.0688

$C_{16}H_{19}NSe$ Requires: 305.0683

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

1-t-Butyl-7,8,9,10-tetrahydrocyclohept[hi]-indolizine-2-carboselenaldehyde (285g)

Phenylphosphonoselenoic dichloride (258) (3.75ml of approx.2M in xylene, approx. 7.5mmol) was added to a stirred solution of 1-t-butyl-7,8,9,10-tetrahydrocyclohept[hi]indolizine-2-carbaldehyde (276g) (1.2768g, 5mmol) in dichloromethane (100ml). The solution was stirred at ambient temperature for 10 minutes, then dichloromethane (400ml) added. The solution was washed with aqueous sodium hydroxide solution (250ml of 0.5M) and then with water (2 x 400ml). The solution was dried and evaporated at ambient temperature, and then benzene (50ml) added to the residue. This was in turn evaporated and the residue extracted with aliquots of warm benzene (100ml in total). The combined extracts were cooled to ambient temperature and chromatographed without further evaporation on alumina (35 x 2.6cm) using benzene as eluant. Initial yellow eluates were discarded, and the eluant changed to benzene/ether (9:1). Green eluates were evaporated at ambient temperature and then dissolved in dichloromethane (10ml).

After filtration, the solution was rapidly reduced to approximately 3ml in volume on the water-bath and warm n-hexane (50ml) added. The solution was allowed to crystallise and the precipitate washed once with n-hexane to afford 1-t-butyl-7,8,9,10-tetrahydrocyclohept[hi]-indolizine-2-carboselenaldehyde (285g), clusters of ochre microneedles (0.3438g, 21.6%), m.pt. 163°-165°C, with slight decomposition from 161°C. A second crop afforded clusters of ochre microneedles (0.2959g, 18.6 %) from n-hexane. The total yield was thus (0.6397g, 40.2%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{17}H_{21}NSe$ MW = 318.31(96)

Microanalysis	Found:	63.89 %C	6.51 %H	4.11 %N
$C_{17}H_{21}NSe$	Requires:	64.15 %C	6.65 %H	4.40 %N

Accurate mass at $m^{+\cdot}$ 319	Found:	319.0817
$C_{17}H_{21}NSe$	Requires:	319.0839

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

C. Synthesis Of Pentacarbonyl(indolizine-3-carboselenaldehyde-Se)tungsten(0) Complexes (290)

Pentacarbonyl(2,7-dimethylindolizine-3-carboselenaldehyde-Se)tungsten(0) (290a)

Tetraethylammonium pentacarbonyliodotungstate(0) (291) (1.2783g, 2.2mmol) and 2,7-dimethylindolizine-3-carbaldehyde (276a) (0.3464g, 2mmol) were dissolved in dichloromethane (100ml). Phenylphosphonoselenoic dichloride (258) (1.5ml of approx. 2M in xylene, approx. 3mmol) was added, and the solution stirred at ambient temperature for 10 minutes. Dichloromethane (300ml) was added and the solution washed with aqueous sodium hydroxide (250ml of 0.5M) and then with water (2 x 400ml). The solution was dried and evaporated at ambient temperature. Benzene (50ml) was added, and then evaporated.

The residue was extracted with aliquots of warm benzene (200ml in total), and the extracts chromatographed without further evaporation on silica (35 x 2.6cm) using benzene as eluant. Blue eluates were evaporated at ambient temperature, and the residue dissolved in dichloromethane (20ml). After filtration, the solution was rapidly reduced to approximately 5ml in volume on the water-bath. Warm n-hexane (50ml) was added and the solution reduced in volume slightly before being allowed to cool. The resulting precipitate was filtered and washed once with n-hexane to afford pentacarbonyl(2,7-dimethylindolizine-3-carboselenaldehyde-Se)tungsten(0) (290a), clusters of black microneedles with a metallic purple sheen (0.4182g, 37.3%), decomposition from approx. 170°C. A second crop was obtained in a similar manner, and afforded clusters of black microneedles with a metallic purple sheen (0.0253g, 2.3%). The total yield was thus

(0.4435g, 39.6%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{16}H_{11}NO_5SeW$ MW = 560.07(66)

Microanalysis	Found:	34.41 %C	1.91 %H	2.49 %N
$C_{16}H_{11}NO_5SeW$	Requires:	34.31 %C	1.98 %H	2.50 %N

Accurate mass at $m^{+\cdot}$ 561	Found:	No $m^{+\cdot}$ peak was present.
$C_{16}H_{11}NO_5SeW$	Requires:	560.9310

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

Pentacarbonyl(2-t-butyl-7-methylindolizine-3-carboselenaldehyde-Se)tungsten(0) (290b)

Tetraethylammonium pentacarbonyliodotungstate(0) (291) (1.2783g, 2.2mmol) and 2-t-butyl-7-methylindolizine-3-carbaldehyde (276b) (0.4306g, 2mmol) were dissolved in dichloromethane (100ml). Phenylphosphonoselenoic dichloride (258) (1.5ml of approx. 2M in xylene, approx. 3mmol) was added, and the solution stirred at ambient temperature for 10 minutes. Dichloromethane (300ml) was added and the solution washed with aqueous sodium hydroxide (250ml of 0.5M) and then with water (2 x 400ml). The solution was dried and evaporated at ambient temperature. Benzene (50ml) was added, and then evaporated.

The residue was extracted with aliquots of warm benzene (200ml in total), and the extracts chromatographed without further evaporation on silica (25 x 2.6cm) using benzene as eluant. Blue eluates were evaporated at ambient temperature, and the residue dissolved in dichloromethane (20ml). After filtration, the solution was rapidly reduced to approximately 5ml in volume on the water-bath. Warm n-hexane (50ml) was added and the solution reduced in volume slightly before being allowed to cool. The resulting precipitate was filtered and washed once with n-hexane to afford pentacarbonyl(2-t-butyl-7-methylindolizine-3-carboselenaldehyde-Se)tungsten(0) (290b), black spars with a metallic green sheen (0.6925g, 57.5%), decomposition from approx. 161°C. A second crop was obtained in a similar manner, and afforded black spars with a metallic green sheen (0.0466g, 3.9%). The total yield was thus (0.7391g, 61.4%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{19}H_{17}NO_5SeW$ MW = 602.15(70)

Microanalysis	Found:	38.11 %C	2.84 %H	2.24 %N	13.25 %Se
$C_{19}H_{17}NO_5SeW$	Requires:	37.90 %C	2.84 %H	2.33 %N	13.11 %Se

Accurate mass at $m^{+\cdot}$ 603 Found: No $m^{+\cdot}$ peak was present.

$C_{19}H_{17}NO_5SeW$ Requires: 602.9780

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

Pentacarbonyl(2-t-butyl-1-methylindolizine-3-carboselenaldehyde-Se)tungsten(0) (290c)

Tetraethylammonium pentacarbonyliodotungstate(0) (291) (1.2783g, 2.2mmol) and 2-t-butyl-1-methylindolizine-3-carbaldehyde (276c) (0.4306g, 2mmol) were dissolved in dichloromethane (100ml). Phenylphosphonoselenoic dichloride (258) (1.5ml of approx. 2M in xylene, approx. 3mmol) was added, and the solution stirred at ambient temperature for 10 minutes. Dichloromethane (300ml) was added and the solution washed with aqueous sodium hydroxide (250ml of 0.5M) and then with water (2 x 400ml). The solution was dried and evaporated at ambient temperature. Benzene (50ml) was added, and then evaporated.

The residue was extracted with aliquots of warm benzene (200ml in total), and the extracts chromatographed without further evaporation on silica (25 x 2.6cm) using benzene as eluant. Blue eluates were evaporated at ambient temperature, and the residue dissolved in dichloromethane (20ml). After filtration, the solution was rapidly reduced to approximately 5ml in volume on the water-bath. Warm n-hexane (50ml) was added and the solution reduced in volume slightly before being allowed to cool. The resulting precipitate was filtered and washed once with n-hexane to afford pentacarbonyl(2-t-butyl-1-methylindolizine-3-carboselenaldehyde-Se)tungsten(0) (290c), black microprisms with a metallic sheen (0.7472g, 62.0%), decomposition from approx. 171°C. A second crop was obtained in a similar manner, and afforded black microprisms with a metallic sheen (0.0048g, 0.4%). The total yield was thus (0.7520g, 62.4%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{19}H_{17}NO_5SeW$ MW = 602.15(70)

Microanalysis	Found:	37.93 %C	2.76 %H	2.28 %N
$C_{19}H_{17}NO_5SeW$	Requires:	37.90 %C	2.84 %H	2.33 %N

Accurate mass at $m^{+\cdot}$ 603 Found: No $m^{+\cdot}$ peak was present.

$C_{19}H_{17}NO_5SeW$ Requires: 602.0780

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

Pentacarbonyl(2-t-butyl-8-methylindolizine-3-carboselenaldehyde-Se)tungsten(0) (290d)

Tetraethylammonium pentacarbonyliodotungstate(0) (291) (1.2783g, 2.2mmol) and 2-t-butyl-8-methylindolizine-3-carbaldehyde (276d) (0.4306g, 2mmol) were dissolved in dichloromethane (100ml). Phenylphosphonoselenoic dichloride (258) (1.5ml of approx. 2M in xylene, approx. 3mmol) was added, and the solution stirred at ambient temperature for 10 minutes. Dichloromethane (300ml) was added and the solution washed with aqueous sodium hydroxide (250ml of 0.5M) and then with water (2 x 400ml). The solution was dried and evaporated at ambient temperature. Benzene (50ml) was added, and then evaporated.

The residue was extracted with aliquots of warm benzene (200ml in total), and the extracts chromatographed without further evaporation on silica (25 x 2.6cm) using benzene as eluant. Blue eluates were evaporated at ambient temperature, and the residue dissolved in

dichloromethane (20ml). After filtration, the solution was rapidly reduced to approximately 5ml in volume on the water-bath. Warm n-hexane (50ml) was added and the solution reduced in volume slightly before being allowed to cool. The resulting precipitate was filtered and washed once with n-hexane to afford pentacarbonyl(2-t-butyl-8-methylindolizine-3-carboselenaldehyde-Se)tungsten(0) (290d), black microspars with a dull metallic green sheen (0.3980g, 33.0%), decomposition from approx. 171°C. A second crop was obtained in a similar manner, and afforded black microspars with a dull metallic green sheen (0.0733g, 6.1%). The total yield was thus (0.4713g, 39.1%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{19}H_{17}NO_5SeW$ MW = 602.15(70)

Microanalysis	Found:	37.90 %C	2.77 %H	2.32 %N
$C_{19}H_{17}NO_5SeW$	Requires:	37.90 %C	2.84 %H	2.33 %N

Accurate mass at $m^{+\cdot}$ 603	Found:	No $m^{+\cdot}$ peak was present.
$C_{19}H_{17}NO_5SeW$	Requires:	602.9780

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

Pentacarbonyl(1-t-butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]-quinoline-2-carboselenaldehyde-Se)tungsten(0) (290f)

Tetraethylammonium pentacarbonyliodotungstate(0) (291) (1.2783g, 2.2mmol) and 1-t-butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]quinoline-2-carbaldehyde (276f) (0.4827g, 2mmol) were dissolved in dichloromethane (100ml). Phenylphosphonoselenoic dichloride (258) (1.5ml of approx. 2M in xylene, approx. 3mmol) was added, and the solution stirred at ambient temperature for 10 minutes. Dichloromethane (300ml) was added and the solution washed with aqueous sodium hydroxide (250ml of 0.5M) and then with water (2 x 400ml). The solution was dried and evaporated at ambient temperature. Benzene (50ml) was added, and then evaporated.

The residue was extracted with aliquots of warm benzene (200ml in total), and the extracts chromatographed without further evaporation on silica (25 x 2.6cm) using benzene as eluant. Blue eluates were evaporated at ambient temperature, and the residue dissolved in dichloromethane (40ml). After filtration, the solution was rapidly reduced to approximately 10ml in volume on the water-bath. Warm n-hexane (50ml) was added and the solution reduced in volume slightly before being allowed to cool. The resulting precipitate was filtered and washed once with n-hexane to afford pentacarbonyl(1-t-butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]quinoline-2-carboselenaldehyde-Se)-tungsten(0) (290f), clusters of black microspars with a metallic green sheen (0.7794g, 62.0%), decomposition from approx. 167°C. A second crop was obtained in a similar manner, and afforded clusters of black microspars with a metallic green sheen (0.0120g, 1.0%). The total yield was thus (0.7914g, 63.0%).

The reaction and subsequent work-up were carried out under

reduced-light conditions.

$C_{21}H_{19}NO_5SeW$ MW = 628.19(48)

Microanalysis	Found:	40.02 %C	2.97 %H	2.19 %N	12.70 %Se
$C_{21}H_{19}NO_5SeW$	Requires:	40.15 %C	3.05 %H	2.23 %N	12.57 %Se

Accurate mass at $m^{+\cdot}$ 629 Found: No $m^{+\cdot}$ peak was present.

$C_{21}H_{19}NO_5SeW$ Requires: 628.9936

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

Pentacarbonyl(1,2-dimethylindolizine-3-carboselenaldehyde-Se)tungsten(0) (290j)

Tetraethylammonium pentacarbonyliodotungstate(0) (291) (1.2783g, 2.2mmol) and 1,2-dimethylindolizine-3-carbaldehyde (276j) (0.3464g, 2mmol) were dissolved in dichloromethane (100ml). Phenylphosphonoselenoic dichloride (258) (1.5ml of approx. 2M in xylene, approx. 3mmol) was added, and the solution stirred at ambient temperature for 10 minutes. Dichloromethane (300ml) was added and the solution washed with aqueous sodium hydroxide (250ml of 0.5M) and then with water (2 x 400ml). The solution was dried and evaporated at ambient temperature. Benzene (50ml) was added, and then evaporated.

The residue was extracted with aliquots of warm benzene (200ml in total), and the extracts chromatographed without further evaporation

on silica (35 x 2.6cm) using benzene as eluant. Blue eluates were evaporated at ambient temperature, and the residue dissolved in dichloromethane (20ml). After filtration, the solution was rapidly reduced to approximately 5ml in volume on the water-bath. Warm n-hexane (50ml) was added and the solution reduced in volume slightly before being allowed to cool. The resulting precipitate was filtered and washed once with n-hexane to afford pentacarbonyl(1,2-dimethyl-indolizine-3-carboselenaldehyde-Se)tungsten(0) (290j), black needles with a dull brown sheen (0.5121g, 45.7%), decomposition from approx. 166°C. A second crop was obtained in a similar manner, and afforded clusters of black microneedles with a dull brown sheen (0.1667g, 14.9%). The total yield was thus (0.6788g, 60.6%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{16}H_{11}NO_5SeW$ MW = 560.07(66)

Microanalysis	Found:	34.20 %C	1.91 %H	2.47 %N
$C_{16}H_{11}NO_5SeW$	Requires:	34.31 %C	1.98 %H	2.50 %N

Accurate mass at $m^{+\cdot}$ 561	Found:	No $m^{+\cdot}$ peak was present.
$C_{16}H_{11}NO_5SeW$	Requires:	560.9310

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

D. Attempted Synthesis Of Miscellaneous Selenocarbonyl Compounds

N,N-Dimethylselenoformamide (293)

Phenylphosphonoselenoic dichloride (258) (20ml of approx. 2M in benzene, approx. 40mmol) was added to N,N-dimethylformamide (294) (1.55ml, 20mmol) in benzene (50ml), and the solution heated at reflux for 4 hours. The solution was cooled to ambient temperature and benzene (250ml) added. The solution was washed with water (1 x 250ml), then with aqueous sodium hydroxide (2 x 250ml of 0.5M) and finally with water (2 x 250ml). The solution was dried, evaporated at ambient temperature and the residue chromatographed on alumina (25 x 2.2cm) using benzene as eluant. Traces of yellow eluates were discarded, and the eluant gradually changed to benzene/ether (17:3). Slower running yellow eluates were evaporated at ambient temperature, and the residue distilled under reduced pressure (block temperature 120°C at 1.0mbar pressure). The yellow distillate, N,N-dimethylselenoformamide (293) (0.2042g, 7.5%), was stored under refrigeration.

The reaction and subsequent work-up were carried out under reduced-light conditions.

C_3H_7NSe MW = 136.05(50)

Microanalysis	Found:	26.58 %C	5.23 %H	10.57 %N
C_3H_7NSe	Requires:	26.48 %C	5.19 %H	10.29 %N

Accurate mass at $m^{+\cdot}$ 137	Found:	136.9747
C_3H_7NSe	Requires:	136.9744

^{1}H nmr - see Appendix 1

^{13}C nmr see Appendix 2

Mass spectral data - see Appendix 3

5-Phenyl-3H-1,2-dithiole-3-selone (296)

Phenylphosphonoselenoic dichloride (258) (2ml of approx. 2M in xylene, approx. 4mmol) was added to 5-phenyl-3H-1,2-dithiol-3-one (297) (0.3885g, 2mmol) in benzene (20ml), and the solution heated at reflux for 20 minutes. The solution was cooled to ambient temperature and benzene (250ml) added. The solution was washed with water (1 x 300ml), then with aqueous sodium hydroxide (250ml of 0.5M) and finally with water (2 x 250ml). The solution was dried, evaporated and the residue chromatographed on alumina (30 x 2.2cm) using 60-80 petrol/ benzene (4:1) as eluant. Yellow-orange eluates were evaporated, and afforded 5-phenyl-3H-1,2-dithiole-3-selone (296), orange-brown needles (0.0291g, 5.7%) from ethanol, m.pt. 131°-132°C. A second crop afforded orange-brown needles (0.0097g, 1.9%) from ethanol. The total yield was thus (0.0388g, 7.6%).

$C_9H_6S_2Se$ MW = 257.23(44)

Microanalysis	Found:	41.90 %C	2.38 %H
$C_9H_6S_2Se$	Requires:	42.02 %C	2.35 %H

Accurate mass at $m^{+\cdot}$ 258	Found:	257.9068
$C_9H_6S_2Se$	Requires:	257.9076

^{1}H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

The reaction was repeated under the conditions given below.

Phenylphosphonoselenoic dichloride (258) (2ml of approx. 2M in xylene, approx. 4mmol) was added to 5-phenyl-3H-1,2-dithiol-3-one (297) (0.3885g, 2mmol) in toluene (20ml), and the solution heated at reflux for 20 minutes.

An identical work-up afforded 5-phenyl-3H-1,2-dithiole-3-selone (296), orange-brown needles (0.0488g, 9.5%) from ethanol. A second crop afforded orange-brown needles (0.0092g, 1.8%) from ethanol. The total yield was thus (0.0580g, 11.3%).

The reaction was repeated once more under the conditions given below.

Phenylphosphonoselenoic dichloride (258) (2ml of approx. 2M in xylene, approx. 4mmol) was added to 5-phenyl-3H-1,2-dithiol-3-one (297) (0.3885g, 2mmol) in xylene (20ml), and the solution heated at reflux for 20 minutes.

An identical work-up afforded 5-phenyl-3H-1,2-dithiole-3-selone (296), orange-brown needles (0.0532g, 10.3%) from ethanol. A second crop afforded orange-brown needles (0.0089g, 1.7%) from ethanol. The total yield was thus (0.0621g, 12.1%).

2,6-Dimethyl-4H-pyran-4-selone (299)

Phenylphosphonoselenoic dichloride (258) (2ml of approx. 2M in xylene, approx. 4mmol) was added to 2,6-dimethyl-4H-pyran-4-one (236) (0.2483g, 2mmol) in benzene (20ml), and the solution heated at reflux for 30 minutes. The solution was cooled to ambient temperature and benzene (250ml) added. The solution was washed with water (1 x 250ml), then with aqueous sodium hydroxide (250ml of 0.5M) and finally with water (2 x 250ml). The solution was dried, evaporated at ambient temperature and the residue chromatographed on alumina (25 x 2.8cm) using 60-80 petrol/benzene (4:1) as eluant. Initial traces of yellow eluates were discarded; subsequent green eluates were evaporated and afforded 2,6-dimethyl-4H-pyran-4-selone (299), red microprisms (0.0049g, 1.3%) from being dissolved in the minimum volume of dichloromethane at ambient temperature and precipitated with n-hexane.

The reaction and subsequent work-up were carried out under reduced-light conditions.

C_7H_8OSe MW = 187.09(96)

Mass spectral data - see Appendix 3

The reaction was repeated under the conditions given below.

Phenylphosphonoselenoic dichloride (258) (2ml of approx. 2M in xylene, approx. 4mmol) was added to 2,6-dimethyl-4H-pyran-4-one (236) (0.2483g, 2mmol) in toluene (20ml), and the solution heated at reflux for 30 minutes. The solution was cooled to ambient temperature and benzene (250ml) added. The solution was washed with water (1 x

250ml), then with aqueous sodium hydroxide (250ml of 0.5M) and finally with water (2 x 250ml). The solution was dried, evaporated at ambient temperature and the residue chromatographed on silica (30 x 2.8cm) using benzene as eluant. Traces of yellow eluates were evaporated, but afforded no discernable product. The eluant was gradually changed until benzene/ether (4:1) was being used, but no further product was obtained.

The reaction and subsequent work-up were carried out under reduced-light conditions.

4(1H)-pyridineselone (300)

Phenylphosphonoselenoic dichloride (258) (2ml of approx. 2M in benzene, approx. 4mmol) was added to a solution of 4-hydroxypyridine (301) (0.1902g, 2mmol) in acetonitrile (20ml), and the solution heated at reflux for 15 minutes. The solution was cooled to ambient temperature and benzene (250ml) added. The solution was washed with water (300ml), then with aqueous sodium hydroxide (250ml of 0.5M) and finally with water (2 x 250ml). The solution was dried and evaporated at ambient temperature, but afforded no discernable product.

The reaction and subsequent work-up were carried out under reduced-light conditions.

The reaction was repeated under the conditions given below.

Phenylphosphonoselenoic dichloride (258) (2ml of approx. 2M in benzene, approx. 4mmol) was added to a solution of 4-hydroxypyridine (301) (0.1902g, 2mmol) in acetonitrile (20ml), and the solution

stirred at ambient temperature for 2 hours. Benzene (250ml) was added and the solution washed with water (300ml), then with aqueous sodium hydroxide (250ml of 0.5M) and finally with water (2 x 250ml). The solution was dried and evaporated at ambient temperature. Although a slight trace of material was observed, immediate deposition of selenium occurred and so no product was isolated.

The reactions and subsequent work-up were carried out under reduced-light conditions.

1-Methylpyrrolidine-2-selone (303)

Phenylphosphonoselenoic dichloride (258) (5ml of approx. 2M in xylene, approx. 10mmol) was added to a solution of 1-methylpyrrolidin-2-one (304) (0.48ml, 5mmol) in benzene (25ml), and the solution heated at reflux for 2 hours. Benzene (300ml) was added and the solution washed with water (400ml), then with aqueous sodium hydroxide (2 x 600ml of 0.5M) and finally with water (2 x 400ml). The solution was dried and partially evaporated at ambient temperature until some 20ml of solution remained. This was then chromatographed directly on alumina (10 x 2.6cm) using benzene as eluant. Pale yellow eluates were evaporated at ambient temperature, but rapid deposition of selenium occurred and no characterisable product could be obtained.

The reaction and subsequent work-up were carried out under reduced-light conditions.

The reaction was repeated under the conditions given below.

Phenylphosphonoselenoic dichloride (258) (5ml of approx. 2M in

xylene, approx. 10mmol) was added to a solution of 1-methylpyrrolidin-2-one (304) (0.48ml, 5mmol) in benzene (25ml), and the solution heated at reflux for 2 hours. Benzene (300ml) was added and the solution washed with water (400ml), then with aqueous sodium hydroxide (2 x 600ml of 0.5M) and finally with water (2 x 400ml). The solution was dried and partially evaporated at ambient temperature until some 20ml of solution remained. This was then chromatographed directly on silica (20 x 2.6cm) using benzene as eluant. Yellow eluates were evaporated at ambient temperature, but rapid deposition of selenium occurred and no characterisable product could be obtained.

The reactions and subsequent work-up were carried out under reduced-light conditions.

Hexahydro-2H-azepine-2-selone (305)

Phenylphosphonoselenoic dichloride (258) (5ml of approx. 2M in xylene, approx. 10mmol) was added to a solution of hexahydro-2H-azepin-2-one (306) (0.5658g, 5mmol) in benzene (50ml), and the solution heated at reflux for 1 hour. The solution was cooled to ambient temperature and dichloromethane (250ml) added. The solution was washed with water (500ml), then with aqueous sodium hydroxide (500ml of 0.5M) and finally with water (2 x 500ml). The solution was dried and evaporated at ambient temperature.

The residue was chromatographed on alumina (10 x 2.6cm) using benzene as eluant. Yellow eluates were evaporated at ambient temperature, but rapid deposition of selenium occurred and no characterisable product could be obtained.

The reaction and subsequent work-up were carried out under

reduced-light conditions.

2,4,6-Cycloheptatriene-1-selone (307)

Phenylphosphonoselenoic dichloride (258) (5ml of approx. 2M in xylene, approx. 10mmol) was added to a solution of 2,4,6-cycloheptatrien-1-one (308) (0.48ml, 5mmol) in benzene (25ml), and the solution stirred at ambient temperature for one hour. A precipitate of white needles formed, which was enhanced by the addition of ether (200ml). The precipitate was filtered and washed with ether, but the filtrate rapidly deposited selenium and proved to be extremely hygroscopic. No characterisable product was therefore obtained.

The reaction was repeated under the conditions given below.

Phenylphosphonoselenoic dichloride (258) (5ml of approx. 2M in xylene, approx. 10mmol) was added to a solution of 2,4,6-cycloheptatrien-1-one (308) (0.48ml, 5mmol) in benzene (25ml), and the solution stirred at ambient temperature for one hour. A precipitate of white needles formed, which was filtered and washed with benzene, but the filtrate rapidly deposited selenium and proved to be extremely hygroscopic. No characterisable product was therefore obtained.

The reactions and subsequent work-ups were carried out under reduced-light conditions, and under an inert atmosphere of nitrogen in a dry-box.

E. Attempted Synthesis Of Miscellaneous Pentacarbonyl(selone-Se)tungsten(0) Complexes

Pentacarbonyl(2,6-dimethyl-4H-pyran-4-selone-Se)tungsten(0) (309)

Phenylphosphonoselenoic dichloride (258) (1.5ml of approx. 2M in xylene, approx. 3mmol) was added to a mixture of 2,6-dimethyl-4H-pyran-4-one (236) (0.2483g, 2mmol) and tetraethylammonium pentacarbonyliodotungstate(0) (291) (1.2783g, 2.2mmol) in dichloromethane (100ml), and the solution heated at reflux for 15 minutes. The solution was cooled to ambient temperature and benzene (1000ml) added. The solution was washed with water (1 x 400ml), then with aqueous sodium hydroxide (400ml of 0.5M) and finally with water (2 x 400ml). The solution was dried, evaporated at ambient temperature and the residue chromatographed on alumina (30 x 2.8cm) using benzene as eluant. Claret eluates were evaporated and afforded red microprisms (0.0053g, 0.5%) from being dissolved in the minimum volume of dichloromethane at ambient temperature and precipitated with n-hexane.

Mass spectral data indicated that both the compounds 2,6-dimethyl-4H-pyran-4-selone (299) and 2,2',6,6'-tetramethyl-4,4'-bipyranylidene (310) were present, but that no pentacarbonyl(2,6-dimethyl-4H-pyran-4-selone-Se) tungsten(0) (309) was present.

The reaction and subsequent work-up were carried out under reduced-light conditions.

C_7H_8OSe MW = 187.09(96)

$C_{14}H_{16}O_2$ MW = 216.279(2)

Mass spectral data - see Appendix 3

Pentacarbonyl(2,4,6-cycloheptatriene-1-selone-Se)tungsten(0) (312)

Tetraethylammonium pentacarbonyliodotungstate(0) (291) (1.2783g, 2.2mmol) was dissolved in dichloromethane (100ml). 2,4,6-Cycloheptatrien-1-one (308) (0.193ml, 2mmol) was added under an atmosphere of argon, and the solution stirred to ensure homogeniety. Phenylphosphonoselenoic dichloride (258) (1.5ml of approx. 2M in xylene, approx. 3mmol) was added, and the solution stirred at ambient temperature for one hour. Dichloromethane (300ml) was added and the solution washed with aqueous sodium hydroxide (250ml of 0.5M) and then with water (2 x 400ml). The solution was dried and evaporated at ambient temperature. Benzene (50ml) was added, and then evaporated.

The residue was extracted with aliquots of warm benzene (100ml in total), and the extracts chromatographed without further evaporation on silica (25 x 2.6cm) using benzene as eluant. Blue eluates were evaporated at ambient temperature, and the residue dissolved in dichloromethane (10ml). After filtration, the solution was rapidly reduced to approximately 3ml in volume on the water-bath. Warm n-hexane (50ml) was added and the solution allowed to cool. The resulting precipitate was filtered and washed once with n-hexane to afford pentacarbonyl(2,4,6-cycloheptatriene-1-selone-Se)tungsten(0) (312), bronze plates (0.0379g, 3.8%), decomposition from approx. 145°C. A second crop was obtained in a similar manner, and afforded bronze microneedles (0.0051g, 0.5%). The total yield was thus (0.0430g, 4.4%).

The reaction and subsequent work-up were carried out under

reduced-light conditions.

$C_{12}H_6O_5SeW$ MW = 492.98(64)

Microanalysis	Found:	28.15 %C	1.15 %H
$C_{12}H_6O_5SeW$	Requires:	29.24 %C	1.23 %H

Accurate mass at $m^{+\cdot}$ 494	Found:	No $m^{+\cdot}$ peak was present.
$C_{12}H_6O_5SeW$	Requires:	493.8888

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

F. Reaction Of Indolizine-3-carbaldehydes (276) With The Reagent Formed By The Reaction Of Phenyldichlorophosphine (259) With Tetramethylammonium Selenocyanate (262)

Reaction With 2,7-Dimethylindolizine-3-carbaldehyde (276a)

Dichlorophenylphosphine (259) (0.825ml, 6.25mmol) was added to a solution of tetramethylammonium selenocyanate (262) (2.3290g, 13mmol) in acetonitrile (75ml), and the solution stirred at ambient temperature for 15 minutes. A solution of 2,7-dimethylindolizine-3-carbaldehyde (276a) (0.8661g, 5mmol) in acetonitrile (25ml) was added, and the solution stirred at ambient temperature for 10 minutes.

Dichloromethane (800ml) was added and the solution washed with aqueous sodium hydroxide (400ml of 0.5M). The aqueous layer was further extracted with dichloromethane (2 x 200ml), and the combined dichloromethane extracts washed with water (600ml). The solution was dried and evaporated, and benzene (50ml) added to the residue. This was then evaporated, and the residue extracted with aliquots of benzene (200ml in total).

After filtration, the filtrate was chromatographed without further evaporation on alumina (35 x 2.6cm) using benzene as eluant. Initial traces of yellow eluates were discarded, and the eluant changed to benzene/ether (9:1). Green eluates were evaporated and then dissolved in dichloromethane (10ml). After filtration, the solution was rapidly reduced to approximately 3ml in volume on the water-bath, and warm n-hexane (50ml) added. The solution was allowed to crystallise, and the precipitate washed once with n-hexane to afford 2,7-dimethylindolizine-3-carboselenaldehyde (285a), green

needles (0.1810g, 15.3%). A second crop afforded green needles (0.0514g, 4.4%) from n-hexane. The total yield was thus (0.2324g, 19.7%).

The product was identified by comparison with an authentic sample, using ^{1}H nmr data and m.pt. and mixed m.pt. determinations.

The residue from the benzene extraction and subsequent filtration was dissolved in boiling dichloromethane (600ml). The solution was cooled to ambient temperature and chromatographed without further evaporation on silica (30 x 4.5cm) using dichloromethane as eluant. Initial traces of yellow eluates were discarded, and the eluant changed to dichloromethane/acetonitrile (9:1). Wine-red eluates were partially evaporated, and filtered to afford 3-(2,7-dimethylindolizin-3-yl)-2,5-dihydro-2-selenoformyl-1,2,4-selenadiazole-5-selone (315a), black microprisms (0.0321g, 1.4%), m.pt. 121°-125°C. Further partial evaporation of the solution afforded a second crop, black microprisms (0.0417g, 1.9%). Acetonitrile (200ml) was added and the solution partially evaporated, but no more product was afforded. The total yield was thus (0.0738g, 3.3%).

The reaction and subsequent work-up were carried out under reduced-light conditions, but considerable decomposition of dark blue material occurred during the above procedure.

$C_{13}H_{11}N_3Se_3$ MW = 446.13(00)

Microanalysis	Found:	35.29 %C	2.54 %H	9.17 %N
$C_{13}H_{11}N_3Se_3$	Requires:	35.00 %C	2.48 %H	9.42 %N

Accurate mass at $m^{+\cdot}$ 449 Found: No $m^{+\cdot}$ peak was present.

$C_{13}H_{11}N_3Se_3$ Requires: 448.8449

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

Reaction With 2-t-Butyl-7-methylindolizine-3-carbaldehyde (276b)

Dichlorophenylphosphine (259) (0.825ml, 6.25mmol) was added to a solution of tetramethylammonium selenocyanate (262) (2.3290g, 13mmol) in acetonitrile (75ml), and the solution stirred at ambient temperature for 15 minutes. A solution of 2-t-butyl-7-methylindolizine-3-carbaldehyde (276b) (1.0765g, 5mmol) in acetonitrile (25ml) was added, and the solution stirred at ambient temperature for 10 minutes.

Dichloromethane (800ml) was added and the solution washed with aqueous sodium hydroxide (400ml of 0.5M). The aqueous layer was further extracted with dichloromethane (2 x 200ml), and the combined dichloromethane extracts washed with water (600ml). The solution was dried and evaporated, and benzene (50ml) added to the residue. This was then evaporated, and the residue extracted with aliquots of benzene (200ml in total).

After filtration, the filtrate was chromatographed without further evaporation on alumina (35 x 2.6cm) using benzene as eluant. Initial yellow eluates were discarded, and the eluant changed to benzene/ether (9:1). Green eluates were evaporated and then dissolved in dichloromethane (10ml). After filtration, the solution was rapidly reduced to approximately 3ml in volume on the water-bath, and warm

n-hexane (50ml) added. The solution was allowed to crystallise, and the precipitate washed once with n-hexane to afford 2-t-butyl-7-methylindolizine-3-carboselenaldehyde (285b), purple plates (0.4683g, 33.7%). A second crop afforded purple microcrystals (0.0390g, 2.8%) from n-hexane. The total yield was thus (0.5073g, 36.5%).

The product was identified by comparison with an authentic sample, using ^{1}H nmr data and m.pt. and mixed m.pt. determinations.

The residue from the benzene extraction and subsequent filtration was dissolved in boiling dichloromethane (600ml). The solution was cooled to ambient temperature and chromatographed without further evaporation on silica (30 x 4.5cm) using dichloromethane as eluant. Initial yellow eluates were discarded, and the eluant changed to dicloromethane/acetonitrile (9:1). Purple eluates were partially evaporated, and filtered to afford 3-(2-t-butyl-7-methylindolizin-3-yl)-2,5-dihydro-2-selenoformyl-1,2,4-selenadiazole-5-selone (315b), very dark purple, almost black, microspars with a dull green sheen (0.5485g, 22.5%), m.pt. 169°-172°C. Further partial evaporation of the solution afforded a second crop, very dark purple, almost black, microspars with a dull green sheen (0.0404g, 1.7%). Acetonitrile (200ml) was added and the solution partially evaporated, but no more product was afforded. The total yield was thus (0.5889g, 24.1%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{16}H_{17}N_3Se_3$ MW = 488.21(04)

Microanalysis	Found:	39.55 %C	3.48 %H	8.45 %N	48.45 %Se
$C_{16}H_{17}N_3Se_3$	Requires:	39.36 %C	3.51 %H	8.61 %N	48.52 %Se

Accurate mass at $m^{+\cdot}$ 491 Found: No $m^{+\cdot}$ peak was present.

$C_{16}H_{17}N_3Se_3$ Requires: 490.8918

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

Reaction With 2-t-Butyl-1-methylindolizine-3-carbaldehyde (276c)

Dichlorophenylphosphine (259) (0.825ml, 6.25mmol) was added to a solution of tetramethylammonium selenocyanate (262) (2.3290g, 13mmol) in acetonitrile (75ml), and the solution stirred at ambient temperature for 15 minutes. A solution of 2-t-butyl-1-methylindolizine-3-carbaldehyde (276c) (1.0765g, 5mmol) in acetonitrile (25ml) was added, and the solution stirred at ambient temperature for 10 minutes.

Dichloromethane (800ml) was added and the solution washed with aqueous sodium hydroxide (400ml of 0.5M). The aqueous layer was further extracted with dichloromethane (2 x 200ml), and the combined dichloromethane extracts washed with water (600ml). The solution was dried and evaporated, and benzene (50ml) added to the residue. This was then evaporated, and the residue extracted with aliquots of benzene (200ml in total).

After filtration, the filtrate was chromatographed without further evaporation on alumina (35 x 2.6cm) using benzene as eluant. Initial traces of yellow eluates were discarded, and the eluant

changed to benzene/ether (9:1). Green eluates were evaporated and then dissolved in dichloromethane (10ml). After filtration, the solution was rapidly reduced to approximately 3ml in volume on the water-bath, and warm n-hexane (50ml) added. The solution was allowed to crystallise, and the precipitate washed once with n-hexane to afford 2-t-butyl-1-methylindolizine-3-carboselenaldehyde (285c), green needles (0.4455g, 32.0%). A second crop afforded green needles (0.0180g, 1.3%) from n-hexane. The total yield was thus (0.4635g, 33.3%).

The product was identified by comparison with an authentic sample, using ^{1}H nmr data and m.pt. and mixed m.pt. determinations.

The residue from the benzene extraction and subsequent filtration was dissolved in boiling dichloromethane (600ml). The solution was cooled to ambient temperature and chromatographed without further evaporation on silica (30 x 4.5cm) using dichloromethane as eluant. Initial yellow eluates were evaporated to afford a trace of a green product which rapidly decomposed, depositing selenium. The eluant was then changed to dichloromethane/acetonitrile (9:1). Purple eluates were partially evaporated, and filtered to afford 3-(2-t-butyl-1-methylindolizin-3-yl)-2,5-dihydro-2-selenoformyl-1,2,4-selenadiazole-5-selone (315c), black microspars (0.2908g, 11.9%), m.pt. 179°-181°C. Further partial evaporation of the solution afforded a second crop, black microspars (0.3600g, 14.8%). Acetonitrile (200ml) was added and the solution partially evaporated, but no more product was afforded. The total yield was thus (0.6508g, 26.7%).

The reaction and subsequent work-up were carried out under

reduced-light conditions.

$C_{16}H_{17}N_3Se_3$ MW = 488.21(04)

Microanalysis	Found:	38.73 %C	3.32 %H	8.58 %N
$C_{16}H_{17}N_3Se_3$	Requires:	39.36 %C	3.51 %H	8.61 %N

Accurate mass at $m^{+\cdot}$ 491	Found:	No $m^{+\cdot}$ peak was present.
$C_{16}H_{17}N_3Se_3$	Requires:	490.8918

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

Reaction With 2-t-Butyl-8-methylindolizine-3-carbaldehyde (276d)

Dichlorophenylphosphine (259) (0.825ml, 6.25mmol) was added to a solution of tetramethylammonium selenocyanate (262) (2.3290g, 13mmol) in acetonitrile (75ml), and the solution stirred at ambient temperature for 15 minutes. A solution of 2-t-butyl-8-methylindolizine-3-carbaldehyde (276d) (1.0765g, 5mmol) in acetonitrile (25ml) was added, and the solution stirred at ambient temperature for 10 minutes.

Dichloromethane (800ml) was added and the solution washed with aqueous sodium hydroxide (400ml of 0.5M). The aqueous layer was further extracted with dichloromethane (2 x 200ml), and the combined dichloromethane extracts washed with water (600ml). The solution was dried and evaporated, and benzene (50ml) added to the residue. This was then evaporated, and the residue extracted with aliquots of

benzene (200ml in total).

After filtration, the filtrate was chromatographed without further evaporation on alumina (35 x 2.6cm) using benzene as eluant. Initial traces of yellow eluates were discarded, and the eluant changed to benzene/ether (9:1). Green eluates were evaporated and then dissolved in dichloromethane (10ml). After filtration, the solution was rapidly reduced to approximately 3ml in volume on the water-bath, and warm n-hexane (50ml) added. The solution was allowed to crystallise, and the precipitate washed once with n-hexane to afford 2-t-butyl-8-methylindolizine-3-carboselenaldehyde (285d), olive green microspars (0.3358g, 24.1%). A second crop afforded olive green microspars (0.0504g, 3.6%) from n-hexane. The total yield was thus (0.3862g, 27.8%).

The product was identified by comparison with an authentic sample, using ^{1}H nmr data and m.pt. and mixed m.pt. determinations.

The residue from the benzene extraction and subsequent filtration was dissolved in boiling dichloromethane (600ml). The solution was cooled to ambient temperature and chromatographed without further evaporation on silica (30 x 4.5cm) using dichloromethane as eluant. Initial yellow eluates were discarded, and the eluant changed to dichloromethane/acetonitrile (9:1). Purple eluates were partially evaporated, and filtered to afford 3-(2-t-butyl-8-methylindolizin-3-yl)-2,5-dihydro-2-selenoformyl-1,2,4-selenadiazole-5-selone (315d), green spars (0.0303g, 1.2%), m.pt. 170°-173°C. Further partial evaporation of the solution afforded a second crop, green microprisms (0.1381g, 5.7%). Acetonitrile (200ml) was added and the solution

partially evaporated to afford green microprisms (0.4755g, 19.5%). Further partial evaporation afforded no more product. The total yield was thus (0.6439g, 26.4%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{16}H_{17}N_3Se_3$ MW = 488.21(04)

Microanalysis	Found:	38.90 %C	3.37 %H	8.59 %N
$C_{16}H_{17}N_3Se_3$	Requires:	39.36 %C	3.51 %H	8.61 %N

Accurate mass at $m^{+\cdot}$ 491	Found:	No $m^{+\cdot}$ peak was present.
$C_{16}H_{17}N_3Se_3$	Requires:	490.8918

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

Reaction With 1-t-Butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]-quinoline-2-carbaldehyde (276f)

Dichlorophenylphosphine (259) (0.825ml, 6.25mmol) was added to a solution of tetramethylammonium selenocyanate (262) (2.3290g, 13mmol) in acetonitrile (75ml), and the solution stirred at ambient temperature for 15 minutes. A solution of 1-t-butyl-8,9-dihydro-7H-pyrrolo-[3,2,1-ij]quinoline-2-carbaldehyde (276f) (1.2067g, 5mmol) in acetonitrile (50ml) was added, and the solution stirred at ambient temperature for 10 minutes.

Dichloromethane (800ml) was added and the solution washed with aqueous sodium hydroxide (400ml of 0.5M). The aqueous layer was further extracted with dichloromethane (2 x 200ml), and the combined dichloromethane extracts washed with water (600ml). The solution was dried and evaporated, and benzene (50ml) added to the residue. This was then evaporated, and the residue extracted with aliquots of benzene (200ml in total).

After filtration, the filtrate was chromatographed without further evaporation on alumina (35 x 2.6cm) using benzene as eluant. Initial traces of yellow eluates were discarded, and the eluant changed to benzene/ether (9:1). Green eluates were evaporated and then dissolved in dichloromethane (10ml). After filtration, the solution was rapidly reduced to approximately 3ml in volume on the water-bath, and warm n-hexane (50ml) added. The solution was allowed to crystallise, and the precipitate washed once with n-hexane to afford 1-t-butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]quinoline-2-carboselenaldehyde (285f), green microneedles (0.5558g, 36.5%). A second crop afforded green microneedles (0.1120g,7.4%) from n-hexane. The total yield was thus (0.6678g, 43.9).

The product was identified by comparison with an authentic sample, using ^{1}H nmr data and m.pt. and mixed m.pt. determinations.

The residue from the benzene extraction and subsequent filtration was diisolved in boiling dichloromethane (600ml). The solution was cooled to ambient temperature and chromatographed without further evaporation on silica (20 x 4.5cm) using dichloromethane as eluant. Initial traces of yellow eluates were discarded, and the eluant

changed to dichloromethane/acetonitrile (9:1). Purple eluates were partially evaporated, and filtered to afford 3-(1-t-butyl-8,9-dihydro-7H-pyrrolo[3,2,1-ij]quinolin-2-yl)-2,5-dihydro-2-selenoformyl-1,2,4-selenadiazole-5-selone (315f), dark green microprisms (0.2635g, 10.3%), m.pt. 172°-174°C. Further partial evaporation of the solution afforded a second crop, dark green microprisms (0.2291g, 8.9%). Acetonitrile (200ml) was added and the solution partially evaporated, but no more product was afforded. The total yield was thus (0.4926g, 19.2%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{18}H_{19}N_3Se_3$ MW = 514.24(82)

Microanalysis	Found:	41.69 %C	3.59 %H	8.10 %N
$C_{18}H_{19}N_3Se_3$	Requires:	42.04 %C	3.72 %H	8.17 %N

Accurate mass at $m^{+\cdot}$ 517	Found:	No $m^{+\cdot}$ peak was present.
$C_{18}H_{19}N_3Se_3$	Requires:	516.9075

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

Mass spectral data - see Appendix 3

Reaction With 1,2-Dimethylindolizine-3-carbaldehyde (276j)

Dichlorophenylphosphine (259) (0.825ml, 6.25mmol) was added to a solution of tetramethylammonium selenocyanate (262) (2.3290g, 13mmol)

in acetonitrile (75ml), and the solution stirred at ambient temperature for 15 minutes. A solution of 1,2-dimethylindolizine-3-carbaldehyde (276j) (0.8661g, 5mmol) in acetonitrile (25ml) was added, and the solution stirred at ambient temperature for 10 minutes.

Dichloromethane (800ml) was added and the solution washed with aqueous sodium hydroxide (400ml of 0.5M). The aqueous layer was further extracted with dichloromethane (2 x 200ml), and the combined dichloromethane extracts washed with water (600ml). The solution was dried and evaporated, and benzene (50ml) added to the residue. This was then evaporated, and the residue extracted with aliquots of benzene (200ml in total).

After filtration, the filtrate was chromatographed without further evaporation on alumina (35 x 2.6cm) using benzene as eluant. Initial traces of yellow eluates were discarded, and the eluant changed to benzene/ether (9:1). Green eluates were evaporated and then dissolved in dichloromethane (10ml). After filtration, the solution was rapidly reduced to approximately 3ml in volume on the water-bath, and warm n-hexane (50ml) added. The solution was allowed to crystallise, and the precipitate washed once with n-hexane to afford 1,2-dimethylindolizine-3-carboselenaldehyde (285j), brown needles (0.4660g, 39.5%). A second crop afforded brown needles (0.0469g, 4.0%) from n-hexane. The total yield was thus (0.5129g, 43.4%).

The product was identified by comparison with an authentic sample, using ^{1}H nmr data and m.pt. and mixed m.pt. determinations.

The residue from the benzene extraction and subsequent filtration

was dissolved in boiling dichloromethane (800ml). The solution was cooled to ambient temperature and chromatographed without further evaporation on silica (25 x 4.5cm) using dichloromethane as eluant. Initial traces of yellow eluates were discarded, and the eluant changed to dichloromethane/acetonitrile (9:1). Purple eluates were partially evaporated, and filtered to afford 3-(1,2-dimethylindolizin-3-yl)-2,5-dihydro-2-selenoformyl-1,2,4-selenadiazole-5-selone (315j), black microspars with a metallic lustre (0.3746g, 16.8%), m.pt. 186°-189°C. Further partial evaporation of the solution afforded a second crop, black microspars (0.1666g, 7.5%). Acetonitrile (200ml) was added and the solution partially evaporated to afford black microspars (0.0572g, 2.6%). Further partial evaporation afforded no more product. The total yield was thus (0.5984g, 26.8%).

The reaction and subsequent work-up were carried out under reduced-light conditions.

$C_{13}H_{11}N_3Se_3$ MW = 446.13(00)

Microanalysis	Found:	34.27 %C	2.38 %H	9.17 %N	52.50 %Se[250]	
$C_{13}H_{11}N_3Se_3$	Requires:	35.00 %C	2.48 %H	9.42 %N	53.10 %Se	

Accurate mass at $m^{+\cdot}$ 449 Found: No $m^{+\cdot}$ peak was present.

$C_{13}H_{11}N_3Se_3$ Requires: 448.8449

^1H nmr - see Appendix 1

^{13}C nmr - see Appendix 2

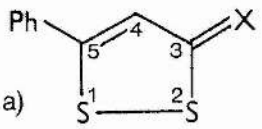
Mass spectral data - see Appendix 3

APPENDIX 1

^{1}H Nmr Data

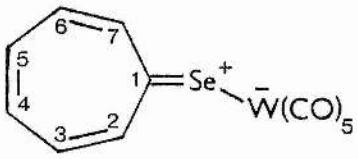
Chemical shift data are given as δ values in ppm downfield from the tetramethylsilane signal. Unless otherwise stated, spectra were obtained using a Bruker WP80 spectrometer, samples were dissolved in deuterated trichloromethane and solution strengths were 0.4 M. Coupling constants are given in Hz where obtained. Assignments refer to the diagrams a),b),....,m).

a)



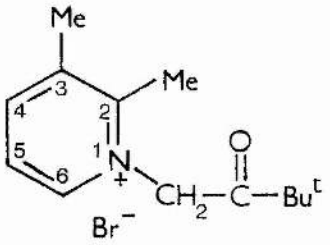
	X
(296)	Se
(298)	S
(297)	O

b)



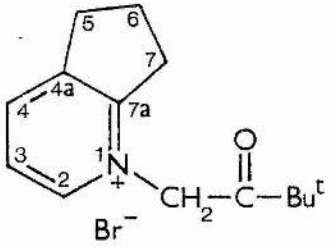
(312)

c)



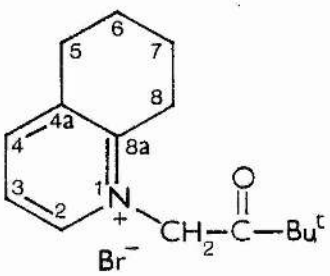
(277d)

d)



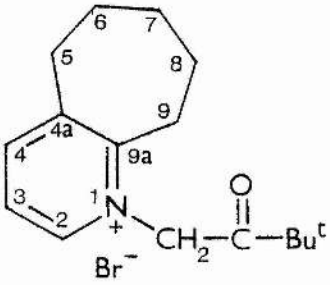
(277e)

e)



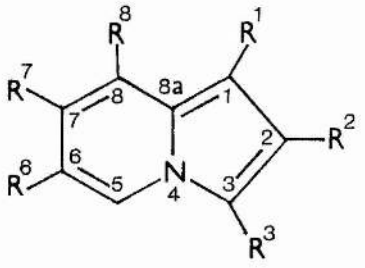
(277f)

f)

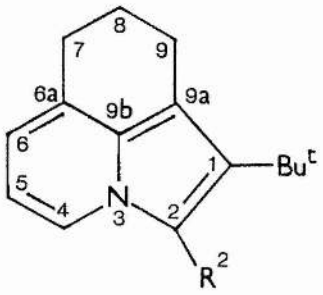


(277g)

g)



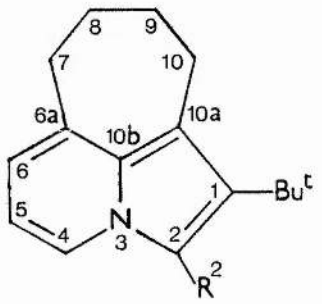
h)



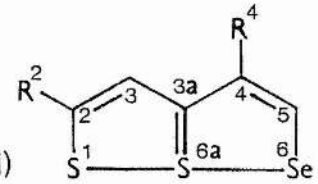
	R^1	R^2	R^3	R^6	R^7	R^8
(280d)	H	t-Bu	H	H	H	Me
(276a)	H	Me	CHO	H	Me	H
(276b)	H	t-Bu	CHO	H	Me	H
(276c)	Me	t-Bu	CHO	H	H	H
(276d)	H	t-Bu	CHO	H	H	Me
(276h)	H	Me	CHO	H	H	H
(276i)	H	t-Bu	CHO	H	H	H
(276j)	Me	Me	CHO	H	H	H
(276k)	H	Me	CHO	Me	H	H
(276l)	H	Me	CHO	H	H	Me
(287c)	Me	t-Bu	CHS	H	H	H
(287j)	Me	Me	CHS	H	H	H
(285a)	H	Me	CHSe	H	Me	H
(285b)	H	t-Bu	CHSe	H	Me	H
(285c)	Me	t-Bu	CHSe	H	H	H
(285d)	H	t-Bu	CHSe	H	H	Me
(285j)	Me	Me	CHSe	H	H	H
(290a)	H	Me	CHSe-$W(CO)_5$	H	Me	H
(290b)	H	t-Bu	CHSe-$W(CO)_5$	H	Me	H
(290c)	Me	t-Bu	CHSe-$W(CO)_5$	H	H	H
(290d)	H	t-Bu	CHSe-$W(CO)_5$	H	H	Me
(290j)	Me	Me	CHSe-$W(CO)_5$	H	H	H

	R^2
(280f)	H
(276f)	CHO
(285f)	CHSe
(290f)	CHSe-$W(CO)_5$

i)



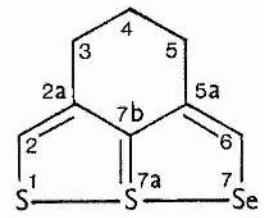
j)



	R^2
(280g)	H
(276g)	CHO
(285g)	CHSe

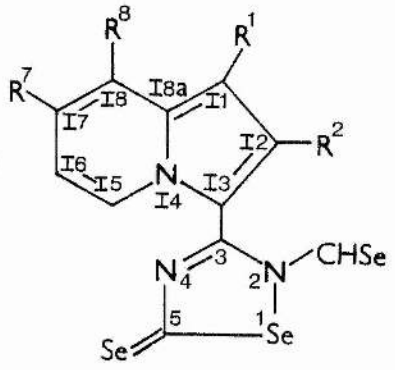
	R^2	R^4
(282a)	Ph	H
(282b)	t-Bu	H
(282c)	Ph	Me

k)



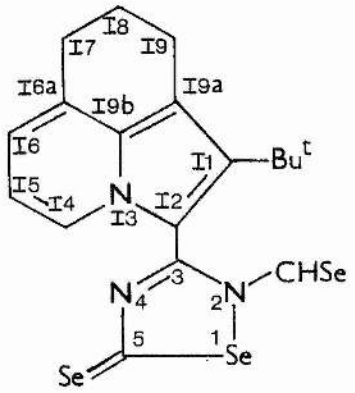
(282d)

l)



	R^1	R^2	R^7	R^8
(315a)	H	Me	Me	H
(315b)	H	t-Bu	Me	H
(315c)	Me	t-Bu	H	H
(315d)	H	t-Bu	H	Me
(315j)	Me	Me	H	H

m)



(315f)

Miscellaneous Compounds

Compound (262)[q]

Signal		1^o Splitting	Proton
1.52	s	-	N-Me4

Compound (262)[p]

Signal		1° Splitting	Proton	2° Splitting
3.14	s	-	N-Me4	t (v)

Compound (293)[q]

Signal		1° Splitting	Proton	2° Splitting
10.63	s	-	CHSe	-
3.35	s	-	?-Me	d J = 0.73
3.32	s	-	?-Me	d J = 0.49

Compound (296)[a,q]

Signal		1° Splitting	Proton
7.77 - 7.43	m	(v)	5-Ph
7.42	s	-	H4

Compound (298)[a]

Signal		1° Splitting	Proton
7.73 - 7.39	m	(v)	5-Ph
7.42	s	-	H4

Compound (297)[a]

Signal		1° Splitting	Proton
7.67 - 7.43	m	(v)	5-Ph
6.83	s	-	H4

Compound (312)[b,n,o,q]

Signal		1° Splitting	Proton
8.46	qn	(v)	H2/7
8.44 - 8.42	m	(v)	H2/7
7.26 - 7.16	m	(v)	H3+4+5+6

Pyridinium Bromide Salts (277)

Compound (277d)[c,p]

Signal		1° Splitting	Proton	2° Splitting	
8.96	d	J(6,5) = 6.35	H6	(u)	(v)
8.52	d	J(4,5) = 8.30	H4	(u)	(v)
7.97	dd	J(5,4) = 7.81			
		J(5,6) = 6.35	H5	-	
6.31	s	-	1-CH_2	-	
2.54	s	-	2Me+3Me	-	
1.29	s	-	t-Bu	-	

Compound (277e)[d,q]

Signal		1° Splitting	Proton
9.43	d	J(2,3) = 5.86	H2
8.28	d	J(4,3) = 8.54	H4
7.80	t	(v)	H3
6.71	s	-	1-CH_2
3.37	t	J(5/7,6) = 8.54	H5/7
3.32	t	J(5/7,6) = 8.50	H5/7
2.36	qn	(v)	H6
1.35	s	-	t-Bu

Compound (277e)[d,p]

Signal		1° Splitting	Proton	2° Splitting	
8.84	d	J(2,3) = 6.10	H2	(u)	(v)
8.53	d	J(4,3) = 7.81	H4	(u)	(v)
8.00	t	(v)	H3	(u)	(v)
6.20	s	-	1-CH_2	-	
3.19	t	J(5+7,6) = ~7.8	H5+7	-	
2.20	qn	(v)	H6	-	
1.28	s	-	t-Bu	-	

Compound (277f)[e,q]

Signal		1° Splitting	Proton	2° Splitting	
9.56	d	J(2,3) = 6.10	H2	(u)	(v)
8.20	d	J(4,3) = 8.06	H4	-	
7.80	t	(v)	H3	(u)	(v)
6.71	s	-	1-CH_2	-	
3.14	br	(u)	H5+8	-	
2.07	br	(u)	H6+7	-	
1.37	s	-	t-Bu	-	

Compound (277f)[e,p]

Signal		1° Splitting	Proton	2° Splitting	
9.01	d	J(2,3) = 7.32	H2	(u)	(v)
8.46	d	J(4,3) = 7.57	H4	(u)	(v)
8.00	t	(v)	H3	(u)	(v)
6.26	s	-	1-CH_2	-	
3.01	br	(u)	H5+8	-	
1.97	br	(u)	H6+7	-	
1.29	s	-	t-Bu	-	

Compound (277g)[f,q]

Signal		1° Splitting	Proton	2° Splitting	
9.53	d	J(2,3) = 6.10	H2	(u)	(v)
8.22	d	J(4,3) = 8.30	H4	(u)	(v)
7.76	dd	(v)	H3	-	
6.86	s	-	1-CH_2	-	
3.17	br	(u)	H5+10	-	
1.92	br	(u)	H6+7+8	-	
1.37	s	-	t-Bu	-	

Compound (277g)[f,p]

Signal		1° Splitting	Proton	2° Splitting	
8.96	d	J(2,3) = 6.10	H2	d	(v)
8.50	d	J(4,3) = 7.81	H4	(u)	(v)
7.94	dd	J(3,4) = 7.57 J(3,2) = 6.35	H3	-	
6.41	s	-	1-CH_2	-	
3.22	br	(u)	H5+10	-	
1.90	br	(u)	H6+7+8	-	
1.29	s	-	t-Bu	-	

Indolizines (280)

Compound (280d)[g,q]

Signal		1° Splitting	Proton	2° Splitting	
7.68	d	J(5/7,6) = 5.61	H5/7	d	(v)
7.11	br	(u)	H5/7	-	
6.37	s	-	H1+3	-	
6.32	dd	J(6,5/7) = 10.99			
		J(6,5/7) = 6.59	H6	-	
2.36	s	-	8-Me	d	J = 0.73
1.35	s	-	t-Bu	-	

Compound (280f)[h,q]

Signal		1° Splitting	Proton	2° Splitting	
7.58	d	J(4/6,5) = 5.86	H4/6	d	(v)
7.01	br	(u)	H4/6	-	
6.26	t	J(5,4+6) = 6.35	H5	-	
6.18	s	-	H2	-	
2.99	t	(v)	H7/9	-	
2.78	t	(v)	H7/9	-	
2.02	qn	(v)	H8	-	
1.36	s	-	t-Bu	-	

Compound (280g)[i,q]

Signal		1° Splitting	Proton	2° Splitting	
7.58	d	J(4/6,5) = 5.61	H4/6	d	J = 2.44
7.05	br	(u)	H4/6	-	
6.23	s	-	H2	-	
6.18	dd	J(5,4/6) = 10.01			
		J(5,4/6) = 6.59	H5	-	
3.10	t	(v)	H5/10	(u)	(v)
2.89	t	(v)	H5/10	(u)	(v)
1.94	t	J(8+9,7/10)=3.17	H8+9	-	
1.38	s	-	t-Bu	-	

Indolizine-3-carbaldehydes (276)

Compound (276b)[g]

Signal		1° Splitting	Proton	2° Splitting
10.17	s	-	CHO	-
9.81	d	J(5,6) = 7.32	H5	-
7.22	br	(u)	H8	t J = 0.98
6.70	d	J(6,5) = 7.32	H6	d (v)
6.26	s	-	H1	-
2.36	s	-	7-Me	-
1.50	s	-	t-Bu	-

Compound (276c)[g]

Signal		1° Splitting	Proton	2° Splitting
10.34	s	-	CHO	-
10.02	d	J(5,6) = 6.84	H5	t J = 1.22
7.46	d	J(8,7) = 9.28	H8	t (v)
7.16	dd	J(7,6) = 6.59		
		J(7,8) = 8.79	H7	d J = 1.22
6.81	dd	J(6,5+7) = 6.83	H6	d J = 1.71
2.43	s	-	1-Me	-
1.61	s	-	t-Bu	-

Compound (276d)[g]

Signal		1° Splitting	Proton	2° Splitting
10.25	s	-	CHO	-
9.80	d	J(5,6) = 6.59	H5	t J = 0.73
6.97	d	J(7,6) = 6.84	H7	t (v)
6.77	t	J(6,5/7) = 6.84		
		J(6,5/7) = 7.08	H6	-
6.37	s	-	H1	d J = 0.73
2.46	s	-	8-Me	d J = 0.73
1.52	s	-	t-Bu	-

Compound (276f)[h]

Signal		1° Splitting	Proton	2° Splitting
10.28	s	-	CHO	-
9.68	d	J(4,5) = 5.86	H4	d (v)
6.80	br	(u)	H5/6	-
6.73	br	(u)	H5/6	-
3.07	t	(v)	H7/9	-
2.85	t	(v)	H7/9	-
2.00	qn	(v)	H8	-
1.58	s	-	t-Bu	-

Compound (276g)[i]

Signal		1° Splitting	Proton	2° Splitting
10.30	s	-	CHO	-
9.90	d	J(4,5) = 6.59	H4	d J = 1.71
6.80	d	(v)	H6	(u) (v)
6.63	dd	J(5,4) = 6.59 J(5,6) = 6.84	H5	-
3.17	t	(v)	H7/10	-
2.99	t	(v)	H7/10	-
2.00	m	(v)	H8+9	-
1.58	s	-	t-Bu	-

1,6a λ^4-Dithia-6-selenapentalenes (282)

Compound (282a)[j]

Signal		1° Splitting	Proton
10.04	d	J(5,4) = 6.84	H5
8.29	s	-	H3
8.05	d	(v)	H4
7.93 - 7.81	m	(v)	2-Ph
7.49 - 7.40	m	(v)	2-Ph

Compound (282b)[j]

Signal		1° Splitting	Proton
10.23	d	J(5,4) = 6.84	H5
8.16	d	J(4,5) = 6.84	H4
7.91	s	-	H3
1.44	s	-	t-Bu

Compound (282c)[j]

Signal		1° Splitting	Proton	2° Splitting
9.43	s	-	H5	qt J = 0.98
8.20	s	-	H3	-
7.94 - 7.82	m	(v)	2-Ph	-
7.49 - 7.38	m	(v)	2-Ph	-
2.60	s	-	4-Me	d J = 0.98

Compound (282d)[k,r]

Signal		1° Splitting	Proton	2° Splitting
9.73	s	-	H6	(u) (v)
8.80	s	-	(H2+6)[r]	-
8.78	s	-	H2	(u) (v)
2.98	t	(v)	H3+5	(u) (v)
2.00	qn	(v)	H4	(u) (v)

Indolizine-3-carboselenaldehydes (285)

Compound (285a)[g,q,s]

Signal		1° Splitting	Proton	2° Splitting
12.09	s	-	CHSe	-
11.80	d	J(5,6) = 6.84	H5	-
7.27	s	-	H8	-
6.92	d	J(6,5) = 7.08	H6	d J = 1.71
6.36	s	-	H1	-
2.33	s	-	2Me+7Me	t J = 0.98

Compound (285b)[g,q,s]

Signal		1° Splitting	Proton	2° Splitting
12.44	s	-	CHSe	-
12.06	d	J(5,6) = 6.84	H5	-
7.31	s	-	H8	(u) (v)
6.94	d	J(6,5) = 7.08	H6	d J = 1.46,1.95
6.42	s	-	H1	-
2.33	s	-	7-Me	-
1.49	s	-	t-Bu	-

Compound (285c)[g,q,s]

Signal		1° Splitting	Proton	2° Splitting
12.67	s	-	CHSe	-
12.36	d	J(5,6) = 6.83	H5	d J = 0.98
7.86	t	(v)	H7	(u) (v)
7.56	d	J(8,7) = 8.30	H8	(u) (v)
7.11	t	J(6,5+7) = 6.84	H6	d J = 1.46
2.37	s	-	1-Me	-
1.61	s	-	t-Bu	-

Compound (285d)[g,q]

Signal		1° Splitting	Proton	2° Splitting
12.78	s	-	CHSe	-
12.01	d	J(5,6) = 6.84	H5	-
7.61	d	J(7,6) = 7.32	H7	t (v)
7.01	t	J(6,5) = 6.84 J(6,7) = 7.32	H6	-
6.52	s	-	H1	-
2.59	s	-	8-Me	-
1.52	s	-	t-Bu	-

Compound (285f)[h,q]

Signal		1° Splitting	Proton	2° Splitting
12.51	s	-	CHSe	-
12.00	d	J(4,5) = 6.84	H4	d J = 0.98
7.54	d	J(6,5) = 7.32	H6	d J = 0.98
6.99	t	J(5,4) = 6.84 J(5,6) = 7.32	H5	-
3.01	t	J(7/9,8) = 6.35	H7/9	-
2.97	t	(v)	H7/9	-
2.00	qn	(v)	H8	-
1.57	s	-	t-Bu	-

Compound (285g)[i,q]

Signal		1° Splitting	Proton
12.54	s	-	CHSe
12.26	d	J(4,5) = 6.84	H4
7.53	d	J(6,5) = 6.84	H6
6.99	t	(v)	H5
3.22 - 3.14	br	(u)	H7+10
2.13 - 1.98	br	(u)	H8+9
1.60	s	-	t-Bu

Compound (285g)[i,n,o,q]

Signal		1° Splitting	Proton	2° Splitting
12.50	s	-	CHSe	-
12.27	d	J(4,5) = 6.65	H4	-
7.57	d	J(6,5) = 7.07	H6	d J = 0.86
7.03	t	J(5,4+6) = 6.99	H5	-
3.17 - 3.12	m	(v)	H7+10	-
2.06 - 1.98	m	(v)	H8+9	-
1.61	s	-	t-Bu	-

Compound (285j)[g,q,s]

Signal		1° Splitting	Proton	2° Splitting
12.16	s	-	CHSe	-
11.99	d	J(5,6) = 6.84	H5	d J = 0.98
7.85	t	J(7,6+8) = 7.81	H7	(u) J = 0.98
7.48	d	J(8,7) = 8.30	H8	(u) (v)
7.09	t	J(6,5+7) = 6.83	H6	d J = 1.46
2.29	s	-	1Me/2Me	-
2.17	s	-	1Me/2Me	-

Pentacarbonyl(indolizine-3-carboselenaldehyde-Se)-tungsten(0) Complexes (290)

Compound (290a)[g,q]

Signal		1° Splitting	Proton	2° Splitting	
10.82	s	-	CHSe	-	
10.70	d	J(5,6) = 7.32	H5	-	
7.39	br	(u)	H8	-	
7.08	d	J(6,5) = 7.32	H6	d	(v)
6.52	br	(u)	H1	-	
2.40	s	-	2Me/7Me	-	
2.35	s	-	2Me/7Me	d	J = 0.98

Compound (290a)[g,o,q]

Signal		1° Splitting	Proton	2° Splitting	
10.70	d	J(5,6) = 6.35	H5	-	
10.68	s	-	CHSe	-	
7.41	br	(u)	H8	-	
7.14	d	J(6,5) = 6.84	H6	d	(v)
6.56	br	(u)	H1	-	
2.41	s	-	2Me/7Me	-	
2.36	s	-	2Me/7Me	d	J = 0.98

Compound (290a)[g,n,o,q]

Signal		1° Splitting	Proton	2° Splitting	
10.71	d	J(5,6) = 6.84	H5	-	
10.67	s	-	CHSe	-	3J(w-h) = 4.22
7.43	s	-	H8	t	J = 0.84
7.16	d	J(6,5) = 6.95	H6	d	J = 1.78
6.58	s	-	H1	-	
2.42	s	-	2Me/7Me	-	
2.38	s	-	2Me/7Me	d	J = 1.04

Compound (290b)[g,o,q]

Signal		1° Splitting	Proton	2° Splitting	
11.06	s	-	CHSe	-	
10.87	d	J(5,6) = 6.84	H5	-	
7.44	br	-	H8	-	
7.16	d	J(6,5) = 6.84	H6	d	(v)
6.61	s	-	H1	-	
2.42	s	-	7-Me	-	
1.50	s	-	t-Bu	-	

Compound (290b)[g,n,o,q]

Signal		1° Splitting	Proton	2° Splitting	
11.04	s	-	CHSe	-	3J(w-h) = 3.97
10.88	d	J(5,6) = 6.76	H5	-	
7.45	s	-	H8	t	J = 0.92
7.18	d	J(6,5) = 6.73	H6	d	J = 1.89
6.61	s	-	H1	-	
2.43	s	-	7-Me	-	
1.51	s	-	t-Bu	-	

Compound (290c)[g,o,q]

Signal		1° Splitting	Proton	2° Splitting	
11.25	s	-	CHSe	-	
11.12	d	J(5,6) = 6.84	H5	t	(v)
8.02	dd	(v)	H7	d	(v)
7.70	d	J(8,7) = 8.79	H8	t	(v)
7.34	t	J(6,5) = 6.84	H6	d	J = 1.46
2.39	s	-	1-Me	-	
1.62	s	-	t-Bu	-	

Compound (290c)[g,n,o,q]

Signal		1° Splitting	Proton	2° Splitting	
11.23	s	-	CHSe	-	3J(w-h) = 3.85
11.12	d	J(5,6) = 6.75	H5	t	J = 0.97
8.03	dd	J(7,6/8) = 7.24			
		J(7,6/8) = 7.22	H7	d	J = 1.09
7.72	d	J(8,7) = 8.56	H8	t	J = 1.11
7.36	t	J(6,5+7) = 6.98	H6	d	J = 1.34
2.41	s	-	1-Me	-	
1.63	s	-	t-Bu	-	

Compound (290d)[g,o,q]

Signal		1° Splitting	Proton
11.33	s	-	CHSe
10.85	d	J(5,6) = 6.84	H5
7.78	d	J(7,6) = 8.30	H7
7.24	t	(v)	H6
6.71	s	-	H1
2.62	s	-	8-Me
1.52	s	-	t-Bu

Compound (290d)[g,n,o,q]

Signal		1° Splitting	Proton	2° Splitting	
11.30	s	-	CHSe	-	3J(w-h) = 4.19
10.86	d	J(5,6) = 6.80	H5	d	J = 0.69
7.78	d	J(7,6) = 7.30	H7	t	J = 0.93
7.26	t	J(6,5+7) = 7.04	H6	-	
6.72	s	-	H1	-	
2.63	s	-	8-Me	-	
1.53	s	-	t-Bu	-	

Compound (290f)[h,n,o,q]

Signal		1° Splitting	Proton	2° Splitting	
11.10	s	-	CHSe	-	3J(w-h) = 3.84
10.86	d	J(4,5) = 6.74	H4	d	J = 0.80
7.72	d	J(6,5) = 7.26	H6	d	J = 0.97
7.26	t	J(5,4+6) = 6.99	H5	-	
3.03	t	J(7/9,8) = 6.24	H7/9	-	
3.01	t	J(7/9,8) = 6.11	H7/9	-	
2.03	qn	J(8,7+9) = 6.24	H8	-	
1.60	s	-	t-Bu	-	

Compound (290j)[g,n,o,q]

Signal		1° Splitting	Proton	2° Splitting
10.88	d	J(5,6) = 6.79	H5	t J = 1.02
10.72	s	-	CHSe	- 3J(w-h) = 4.25
8.01	dd	J(7,6/8) = 7.26		
		J(7,6/8) = 7.24	H7	d J = 1.15
7.65	d	J(8,7) = 8.51	H8	t J = 1.10
7.33	t	J(6,5+7) = 6.96	H6	d J = 1.31
2.32	s	-	1Me/2Me	d J = 0.40
2.20	s	-	1Me/2Me	d J = 0.53

Compounds Proposed To Be 3-(Indolizin-3-yl)-2,5-dihydro-2-selenoformyl-1,2,4-selenadiazole-5-selones (315)

Compound (315a)[l,n,o,q]

Signal		1° Splitting	Proton	2° Splitting
10.12	d	J(5,6) = 6.94	H5	-
8.70	s	-	CHSe	-
7.39	br	(u)	H8	t J = 0.83
7.08	d	J(6,5) = 6.95	H6	d J = 1.78
6.59	s	-	H1	-
2.50 - 2.49	s	-	2Me+7Me	(u) (v)

Compound (315b)[l,o,q]

Signal		1° Splitting	Proton	2° Splitting
10.27	d	J(5,6) = 7.32	H5	-
9.02	s	-	CHSe	-
7.41	s	-	H8	-
7.10	d	J(6,5) = 6.84	H6	d J = 1.46
6.63	s	-	H1	-
2.48	s	-	7-Me	-
1.52	s	-	t-Bu	d J = 0.98

Compound (315b)[1,n,o,q]

Signal		1° Splitting	Proton	2° Splitting
10.28	d	J(5,6) = 6.93	H5	-
9.01	s	-	CHSe	-
7.42	s	-	H8	(u) (v)
7.11	d	J(6,5) = 7.03	H6	d J = 1.84
6.64	s	-	H1	-
2.50	s	-	7-Me	-
1.54	s	-	t-Bu	-

Compound (315c)[1,o,q]

Signal		1° Splitting	Proton
(t)	?	?	H5
9.23	s	-	CHSe
(t)	?	?	H7
(t)	?	?	H8
(t)	?	?	H6
2.45	s	-	1-Me
1.66	s	-	t-Bu

Compound (315c)[1,n,o,q]

Signal		1° Splitting	Proton	2° Splitting
10.55	d	J(5,6) = 6.84	H5	-
9.21	s	-	CHSe	-
7.74	dd	(v)	H7	d (v)
7.66	d	J(8,7) = 8.43	H8	t (v)
7.29	t	J(6,5+7) = 6.91	H6	d (v)
2.46	s	-	1-Me	-
1.66	s	-	t-Bu	-

Compound (315d)[1,o,q]

Signal		1° Splitting	Proton	2° Splitting
10.28	d	J(5,6) = 6.35	H5	-
9.15	s	-	CHSe	-
7.48	d	J(7,6) = 7.08	H7	(u) (v)
7.16	dd	J(6,5) = 6.83 J(6,7) = 7.08	H6	-
6.73	s	-	H1	d J = 0.73
2.55	s	-	8-Me	-
1.55	s	-	t-Bu	-

Compound (315d)[l,n,o,q]

Signal		1° Splitting		Proton	2° Splitting	
10.28	d	J(5,6)	= 7.07	H5	-	
9.14	s	-		CHSe	-	
7.49	d	J(7,6)	= 7.25	H7	(u)	(v)
7.18	dd	J(6,5/7)	= 7.04			
		J(6,5/7)	= 7.07	H6	-	
6.74	s	-		H1	-	
2.56	s	-		8-Me	-	
1.57	s	-		t-Bu	-	

Compound (315f)[m,n,o,q]

Signal		1° Splitting		Proton	2° Splitting	
10.22	d	J(4,5)	= 6.84	H4	-	
9.10	s	-		CHSe	-	
7.44	d	J(6,5)	= 7.19	H6	d	J = 1.00
7.19	dd	J(5,4/6)	= 6.97			
		J(5,4/6)	= 7.02	H5	-	
3.09	t	J(7/9,8)	= 6.22	H7/9	-	
2.94	t	J(7/9,8)	= 6.08	H7/9	-	
2.04	qn	J(8,7+9)	= 6.17	H8	-	
1.63	s	-		t-Bu	-	

Compound(315j)[l,n,o,q]

Signal		1° Splitting		Proton	2° Splitting	
10.33	d	J(5,6)	= 6.75	H5	t	(v)
8.77	s	-		CHSe	-	
7.72	dd	J(7,6/8)	= 7.12			
		J(7,6/8)	= 7.16	H7	d	(v)
7.60	d	J(8,7)	= 8.55	H8	(u)	(v)
7.26	dd	J(6,5/7)	= 6.91			
		J(6,5/7)	= 6.98	H6	d	(v)
2.45	s	-		1Me/2Me	-	
2.25	s	-		1Me/2Me	-	

a,b,....,m - Refer to diagrams a),b),....m).
n - Bruker WH360 Spectrometer.
o - Deuterated dichloromethane.
p - Deuterated dimethylsulphoxide.
q - Saturated solution <0.4 M.
r - Contaminated with 4,5-dihydro-3H-[1,2]dithiolo[4,5,1-hi]-[1,2]benzodithiole-7a-S^4 (283d).
s - Spectrum obtained for authentification purposes.
(t) - Signal not observed.
(u) - Insufficiently resolved to ascertain the degree of splitting.
(v) - Coupling constant unobtainable.

APPENDIX 2

^{13}C Nmr Data

Chemical shift data are given as δ values in ppm downfield from the tetramethylsilane signal. Unless otherwise stated, spectra were obtained using a Varian CFT20 spectrometer, samples were dissolved in deuterated trichloromethane and solution strengths were 2.0 M. $^{1}J_{C-H}$ coupling constants are given in Hz where obtained. Assignments refer to diagrams given in Appendix 1.

Miscellaneous Compounds

Compound (262)[p]

Signal	$^{1}J_{C-H}$	Carbon
116.74	-	SeCN
54.51	143.7	N-Me4

Compound (293)[q]

Signal	$^{1}J_{C-H}$	Carbon
190.01	177.6	CHSe
47.39	(s)	?-Me
40.10	(s)	?-Me

Compound (295)

Signal	$^{1}J_{C-H}$	Carbon
187.64	(t)	CHS
45.23	(t)	?-Me
37.03	(t)	?-Me

Compound (294)

Signal	$^{1}J_{C-H}$	Carbon
162.71	(t)	CHO
35.99	(t)	?-Me
30.91	(t)	?-Me

Compound (296)[a,q]

Signal	$^{1}J_{C-H}$	Carbon
247.73	-	C3
197.34	-	C5
139.63	(t)	C4
133.69	-	5-Ph
131.78	(t)	5-Ph
129.48	(t)	5-Ph
127.02	(t)	5-Ph

Pyridinium Bromide Salts (277)

Compound (277d)[c,p]

Signal	$^1J_{C-H}$	Carbon
206.90	-	C=O
154.92	-	C2
146.20	170.9	C4/6
144.25	(s)	C4/6
138.22	-	C3
124.41	178.4	C5
63.98	144.8	1-CH_2
43.15	-	But(Q)
25.57	127.1	But(Me3)
19.25	(s)	2Me/3Me
16.66	130.6	2Me/3Me

Compound (277e)[d,q]

Signal	$^1J_{C-H}$	Carbon
206.48	-	C=O
162.29	-	C7a
144.99	-	C4a
143.86	188.5	C2/4
141.15	169.0	C2/4
125.48	173.8	C3
64.63	143.5	1-CH_2
43.90	-	But(Q)
32.29	~140	C5/7
31.19	~140	C5/7
26.26	127.7	But(Me3)
22.35	(s)	C6

Compound (277f)[e,q]

Signal	$^1J_{C-H}$	Carbon
206.88	-	C=O
154.67	-	C8a
146.00	170.3	C2/4
145.56	(s)	C2/4
139.16	-	C4a
124.39	175.1	C3
63.78	142.5	1-CH_2
43.94	-	But(Q)
28.90	(s)	C5/8
27.13	(s)	C5/8
26.35	127.8	But(Me3)
21.39	~140	C6/7
20.53	~140	C6/7

Compound (277g)[f,q]

Signal	$^1J_{C-H}$	Carbon
206.98	-	C=O
160.98	-	C9a
145.52	164.0	C2/4
145.23	(s)	C2/4
144.64	-	C4a
125.00	174.7	C3
65.24	144.3	1-CH_2
43.88	-	But(Q)
34.90	(s)	C5/6/7/8/9
31.49	(s)	C5/6/7/8/9
30.82	(s)	C5/6/7/8/9
26.28	127.8	But(Me3)
25.76	(s)	C5/6/7/8/9
24.61	(s)	C5/6/7/8/9

Indolizines (280)

Compound (280d)[g,q]

Signal	$^1J_{C-H}$	Carbon
140.49	-	C2/8/8a
133.66	-	C2/8/8a
127.50	-	C2/8/8a
122.87	(s)	C5
115.80	161.1	C7
109.62	162.4	C3
108.89	~185	C6
95.00	165.2	C1
31.95	125.4	But(Me3)
31.01	-	But(Q)
18.01	127.1	8-Me

Compound (280f)[h,q]

Signal	$^1J_{C-H}$	Carbon
(r)	(s)	?
(r)	(s)	?
136.05	(s)	?
129.96	(s)	?
121.66	177.4	C4/6
110.08	160.6	C5
107.82	-	C9a
107.38	184.2	C2
31.83	-	But(Q)
30.91	125.3	But(Me3)
27.77	(s)	C7/8/9
24.45	(s)	C7/8/9
23.85	(s)	C7/8/9

Compound (280g)[i,q]

Signal	$^1J_{C-H}$	Carbon
137.15	?	?
136.13	?	?
133.83	?	?
122.71	176.0	C2/4/5/6
114.22	168.7	C2/4/5/6
112.51	?	?
108.91	174.1	C2/4/5/6
105.21	?	?
34.78	(s)	C7/8/9/10
31.69	-	But(Q)
30.90	125.3	But(Me3)
29.25	(s)	C7/8/9/10
27.49	(s)	C7/8/9/10
27.03	(s)	C7/8/9/10

Indolizine-3-carbaldehydes (276)

Compound (276a)[g]

Signal	$^1J_{C-H}$	Carbon
174.46	169.6	CHO
139.03	-	C2
137.94	-	C8a
136.16	-	C7
127.69	188.6	C5
120.88	-	C3
116.26	(s)	C6/8
115.62	(s)	C6/8
103.23	176.9	C1
21.23	127.4	7-Me
11.45	127.8	2-Me

Compound (276b)[g]

Signal	$^1J_{C-H}$	Carbon
176.47	170.8	CHO
151.84	-	C2
138.14	-	C8a
136.17	-	C7
128.44	188.9	C5
120.14	-	C3
116.62	160.3	C6/8
116.16	161.8	C6/8
100.89	173.1	C1
32.93	127.0	But(Me3)
32.51	-	But(Q)
21.17	127.4	7-Me

Compound (276c)[g]

Signal	$^1J_{C-H}$	Carbon
178.13	172.9	CHO
145.88	-	C2
137.77	-	C8a
128.72	189.5	C5
124.25	163.7	C7
121.09	-	C3
115.79	164.5	C8
113.60	166.6	C6
109.42	-	C1
34.84	-	But(Q)
33.96	126.1	But(Me3)
11.81	127.1	1-Me

Compound (276d)[g]

Signal	$^1J_{C-H}$	Carbon
177.28	171.5	CHO
151.04	-	C2
137.95	-	C8a
126.98	-	C8
126.77	191.8	C5
124.42	168.1	C7
120.89	-	C3
113.80	165.7	C6
100.14	172.8	C1
33.01	126.0	But(Me3)
32.52	-	But(Q)
17.82	127.7	8-Me

Compound (276f)[h,q]

Signal	$^1J_{C-H}$	Carbon
178.09	172.9	CHO
144.12	-	C1
136.82	-	C9b
129.62	-	C6a
126.54	186.3	C4
121.53	-	C2
120.38	162.9	C6
114.25	163.1	C5
111.97	-	C9a
34.92	-	But(Q)
33.96	126.1	But(Me3)
27.62	(s)	C7/8/9
25.50	(s)	C7/8/9
23.60	(s)	C7/8/9

Compound (276g)[i,q]

Signal	$^1J_{C-H}$	Carbon
178.53	174.3	CHO
144.64	-	C1
139.05	-	C10b
133.82	-	C6a
126.76	190.0	C4
122.95	162.4	C6
121.04	-	C2
118.17	-	C10a
113.53	165.9	C5
34.73	-	But(Q)
33.75	126.1	But(Me3)
30.88	(s)	C7/8/9/10
27.21	~130	C7/8/9/10
26.32	~130	C7/8/9/10
23.90	126.4	C7/8/9/10

Compound (276h)[g,q]

Signal	$^1J_{C-H}$	Carbon
175.23	170.5	CHO
138.46	-	C2/8a
137.64	-	C2/8a
128.16	188.6	C5
125.01	165.2	C7
121.17	-	C3
117.56	166.4	C8
113.23	165.5	C6
104.20	174.4	C1
11.45	127.6	2-Me

Compound (276i)[g,q]

Signal	$^1J_{C-H}$	Carbon
177.32	171.6	CHO
151.53	-	C2
137.66	-	C8a
129.04	189.1	C5
125.00	165.3	C7
(r)	-	C3
117.94	166.1	C8
113.81	167.9	C6
101.83	173.6	C1
33.01	126.0	But(Me3)
32.57	-	But(Q)

Compound (276j)[g]

Signal	$^1J_{C-H}$	Carbon
174.64	170.3	CHO
137.35	-	C8a
134.79	-	C2
128.08	188.3	C5
124.19	165.3	C7
120.51	-	C3
115.74	163.9	C8
112.95	170.1	C6
110.66	-	C1
9.03	126.6	1Me/2Me
7.93	127.4	1Me/2Me

Compound (276k)[g]

Signal	$^1J_{C-H}$	Carbon
174.92	169.9	CHO
137.29	-	C2/8a
137.07	-	C2/8a
128.01	162.5	C7
126.32	186.5	C5
123.08	-	C6
121.01	-	C3
116.90	166.0	C8
103.96	173.3	C1
18.23	127.6	6-Me
11.46	127.8	2-Me

Compound (276l)[g]

Signal	$^1J_{C-H}$	Carbon
175.31	170.3	CHO
138.96	-	C2
137.21	-	C8a
126.70	-	C8
126.04	187.8	C5
124.37	161.9	C7
121.63	-	C3
113.31	166.3	C6
102.67	173.7	C1
17.80	(s)	8-Me
11.50	(s)	2-Me

Indolizine-3-carbothialdehydes (287)

Compound (287c)[g,q]

Signal	$^1J_{C-H}$	Carbon
186.15	162.0	CHS
145.56	-	C2
142.06	-	C3/8a
133.84	-	C3/8a
129.29	166.3	C7
127.89	183.2	C5
116.20	166.6	C6/8
116.08	166.1	C6/8
113.06	-	C1
35.27	-	But(Q)
33.68	126.6	But(Me3)
11.95	127.5	1-Me

Compound (287c)[g,o,q]

Signal	$^1J_{C-H}$	Carbon
187.12	162.1	CHS
145.77	-	C2
142.31	-	C3/8a
134.16	-	C3/8a
129.45	(s)	C7
127.97	(s)	C5
116.49	166.3	C6/8
116.49	166.3	C6/8
113.42	-	C1
35.58	-	But(Q)
33.80	126.4	But(Me3)
12.09	127.5	1-Me

Compound (287j)[g,q]

Signal	$^1J_{C-H}$	Carbon
182.29	161.3	CHS
141.50	-	C2/3/8a
135.23	-	C2/3/8a
134.14	-	C2/3/8a
129.00	166.2	C7
127.54	188.7	C5
115.89	167.0	C6/8
115.52	167.6	C6/8
114.00	-	C1
10.10	127.4	1Me/2Me
8.43	127.1	1Me/2Me

Compound (287j)[g,o,q]

Signal	$^1J_{C-H}$	Carbon
183.54	161.5	CHS
(r)	-	C2/3/8a
135.65	-	C2/3/8a
134.56	-	C2/3/8a
129.19	166.3	C7
127.80	188.6	C5
116.36	166.4	C6/8
115.87	165.7	C6/8
114.32	-	C1
10.28	127.7	1Me/2Me
8.53	127.0	1Me/2Me

Indolizine-3-carboselenaldehydes (285)

Compound (285a)[g,q]

Signal	$^1J_{C-H}$	Carbon
177.51	162.7	CHSe
143.78	-	C3/7
143.34	-	C3/7
140.48	-	C2
139.29	-	C8a
126.43	166.6	C5
118.48	(s)	C6/8
117.75	(s)	C6/8
107.82	170.8	C1
22.36	126.2	7-Me
13.29	127.9	2-Me

Compound (285a)[g,o,q]

Signal	$^1J_{C-H}$	Carbon
177.85	(t)	CHSe
144.17	-	C3/7
143.95	-	C3/7
140.82	-	C2
139.71	-	C8a
126.53	(t)	C5
118.81	(t)	C6/8
118.16	(t)	C6/8
108.16	(t)	C1
22.48	(t)	7-Me
13.45	(t)	2-Me

Compound (285b)[g,q]

Signal	$^1J_{C-H}$	Carbon
179.35	162.6	CHSe
152.07	-	C2
143.60	-	C3/7
143.00	-	C3/7
139.00	-	C8a
126.91	165.8	C5
118.82	(s)	C6/8
118.01	(s)	C6/8
106.25	174.5	C1
33.38	-	But(Q)
31.82	126.3	But(Me3)
22.31	(s)	7-Me

Compound (285b)[g,o,q]

Signal	$^1J_{C-H}$	Carbon
179.61	163.8	CHSe
151.78	-	C2
143.86	-	C3/7
142.95	-	C3/7
138.98	-	C8a
126.54	188.0	C5
118.91	168.0	C6/8
118.29	165.4	C6/8
106.53	175.8	C1
33.46	-	But(Q)
31.83	126.4	But(Me3)
22.42	126.8	7-Me

Compound (285c)[g,q]

Signal	$^1J_{C-H}$	Carbon
181.16	163.0	CHSe
145.48	-	C2
(r)	-	C3
139.27	-	C8a
131.08	167.2	C7
126.69	(s)	C5
117.13	(s)	C6/8
116.74	166.4	C6/8
114.49	-	C1
35.72	-	But(Q)
33.51	126.5	But(Me3)
11.97	127.9	1-Me

Compound (285c)[g,o,q]

Signal	$^1J_{C-H}$	Carbon
181.31	(t)	CHSe
(r)	-	C2
(r)	-	C3
(r)	-	C8a
131.48	(t)	C7
126.73	(t)	C5
117.43	(t)	C6/8
117.15	(t)	C6/8
115.00	-	C1
35.96	-	But(Q)
33.54	(t)	But(Me3)
12.06	(t)	1-Me

Compound (285d)[g,q]

Signal	$^1J_{C-H}$	Carbon
182.57	162.8	CHSe
150.88	-	C2
142.05	-	C3
139.39	-	C8a
130.96	163.3	C7
128.00	-	C8
124.75	188.5	C5
116.75	167.9	C6
104.91	174.6	C1
33.36	-	But(Q)
31.88	126.3	But(Me3)
17.71	128.5	8-Me

Compound (285f)[h,q]

Signal	$^1J_{C-H}$	Carbon
179.41	162.8	CHSe
143.15	-	C1
141.98	-	C2
139.69	-	C9b
130.75	-	C6a
128.29	163.5	C6
124.82	190.0	C4
117.32	167.2	C5
116.81	-	C9a
35.57	-	But(Q)
33.22	126.1	But(Me3)
27.12	(s)	C7/8/9
25.34	(s)	C7/8/9
23.16	(s)	C7/8/9

Compound (285j)[g,q]

Signal	$^1J_{C-H}$	Carbon
176.79	162.5	CHSe
143.16	-	C3
139.99	-	C8a
135.36	-	C2
130.94	166.7	C7
126.46	185.0	C5
116.61	167.2	C6/8
116.61	167.2	C6/8
115.51	-	C1
10.73	128.0	1Me/2Me
8.59	127.6	1Me/2Me

Compound (285j)[g,o,q]

Signal	$^1J_{C-H}$	Carbon
178.34	(t)	CHSe
(r)	-	C3
(r)	-	C8a
(r)	-	C2
131.04	(t)	C7
126.59	(t)	C5
117.08	(t)	C6/8
116.87	(t)	C6/8
(r)	-	C1
10.90	(t)	1Me/2Me
8.63	(t)	1Me/2Me

Pentacarbonyl(Indolizine-3-carboselenaldehyde-Se)-tungsten(0) Complexes (290)

Compound (290a)[g,n,o,q]

Signal	$^1J_{C-H}$	Carbon
202.81	- (u)	Ax C=O
199.31	- (w)	Eq C=O
170.04	(t)	CHSe
147.33	-	C3/7
146.59	-	C3/7
141.00	-	C2/8a
140.33	-	C2/8a
127.79	(t)	C5
120.29	(t)	C6/8
119.11	(t)	C6/8
111.21	(t)	C1
22.43	(t)	7-Me
12.98	(t)	2-Me

Compound (290b)[g,n,o,q]

Signal	$^1J_{C-H}$	Carbon
202.84	- (v)	Ax C=O
199.32	- (w)	Eq C=O
172.29	(t)	CHSe
153.19	-	C2
147.48	-	C7
145.81	-	C3
139.21	-	C8a
128.10	(t)	C5
120.58	(t)	C6/8
119.36	(t)	C6/8
109.78	(t)	C1
33.58	-	But(Q)
31.60	(t)	But(Me3)
22.37	(t)	7-Me

Compound (290c)[g,n,o,q]

Signal	$^1J_{C-H}$	Carbon
202.80	- (v)	Ax C=O
199.29	- (w)	Eq C=O
173.23	(t)	CHSe
146.99	-	C2/3
146.03	-	C2/3
139.61	-	C8a
134.07	(t)	C7
128.03	(t)	C5
118.93	(t)	C6/8
118.43	-	C1
117.90	(t)	C6/8
35.77	-	But(Q)
33.20	(t)	But(Me3)
11.90	(t)	1-Me

Compound (290d)[g,n,o,q]

Signal	$^1J_{C-H}$	Carbon
202.77	- (v)	Ax C=O
199.36	- (w)	Eq C=O
176.18	(t)	CHSe
152.34	-	C2
145.21	-	C3
139.94	-	C8a
134.02	(t)	C7
130.01	-	C8
126.27	(t)	C5
118.71	(t)	C6
108.42	(t)	C1
33.75	-	But(Q)
31.84	(t)	But(Me3)
17.67	(t)	8-Me

Compound (290f)[h,n,o,q]

Signal	$^1J_{C-H}$	Carbon
202.92	- (v)	Ax C=O
199.39	- (w)	Eq C=O
172.44	(t)	CHSe
145.05	-	C2
143.81	-	C1
140.08	-	C9b
132.51	-	C6a
131.35	(t)	C6
126.23	(t)	C4
120.45	-	C9a
119.07	(t)	C5
35.72	-	But(Q)
33.00	(t)	But(Me3)
27.20	(t)	C7/8/9
25.55	(t)	C7/8/9
23.15	(t)	C7/8/9

Compound (290j)[g,n,o,q]

Signal	$^1J_{C-H}$	Carbon
202.82	- (v)	Ax C=O
199.31	- (x)	Eq C=O
169.81	(t)	CHSe
146.50	-	C3
140.72	-	C8a
135.97	-	C2
133.92	(t)	C7
128.12	(t)	C5
119.27	-	C1
118.53	(t)	C6/8
117.86	(t)	C6/8
10.53	(t)	1Me/2Me
8.66	(t)	1Me/2Me

Compounds Proposed To Be 3-(Indolizin-3-yl)-2,5-dihydro-2-selenoformyl-1,2,4-selenadiazole-5-selones (315)

Compound (315a)[1,n,o,q]

Signal	$^1J_{C-H}$	Carbon
203.75	-	C3/5
195.16	-	C3/5
146.23	-	I-C2/7
146.16	(t)	CHSe
146.04	-	I-C2/7
144.32	-	I-C8a
133.64	(t)	I-C5
124.05	-	I-C3
119.34	(t)	I-C6/8
118.31	(t)	I-C6/8
111.96	(t)	I-C1
21.96	(t)	I-7-Me
12.49	(t)	I-2-Me

Compound (315b)[1,n,o,q]

Signal	$^1J_{C-H}$	Carbon
203.55	-	C3/5
194.52	-	C3/5
157.42	-	I-C2
148.18	(t)	CHSe
146.15	-	I-C7/8a
145.35	-	I-C7/8a
134.68	(t)	I-C5
122.83	-	I-C3
119.79	(t)	I-C6/8
118.59	(t)	I-C6/8
110.13	(t)	I-C1
33.42	-	I-But(Q)
32.31	(t)	I-But(Me3)
21.89	(t)	I-7-Me

Compound (315c)[1,n,o,q]

Signal	$^1J_{C-H}$	Carbon
203.52	-	C3/5
194.51	-	C3/5
150.01	-	I-C2
149.33	(t)	CHSe
146.44	-	I-C8a
135.36	(t)	I-C7
132.82	(t)	I-C5
123.69	-	I-C3
118.89	-	I-C1
117.82	(t)	I-C6/8
117.14	(t)	I-C6/8
35.58	-	I-But(Q)
33.55	(t)	I-But(Me3)
12.17	(t)	I-1-Me

Compound (315d)[1,n,o,q]

Signal	$^1J_{C-H}$	Carbon
204.36	-	C3/5
195.20	-	C3/5
156.54	-	I-C2
149.58	(t)	CHSe
144.76	-	I-C8a
132.68	(t)	I-C5/7
132.41	(t)	I-C5/7
129.04	-	I-C8
122.96	-	I-C3
117.46	(t)	I-C6
108.51	(t)	I-C1
33.45	-	I-But(Q)
32.47	(t)	I-But(Me3)
17.69	(t)	I-8-Me

Compound (315f)[m,n,o,q]

Signal	$^1J_{C-H}$	Carbon
(r)	-	C3/5
194.10	-	C3/5
148.89	(t)	CHSe
147.75	-	I-C1
144.75	-	I-C9b
133.14	(t)	I-C6
131.69	-	I-C6a
130.22	(t)	I-C4
124.54	-	I-C2/9a
121.14	-	I-C2/9a
118.14	(t)	I-C5
35.53	-	I-But(Q)
33.41	(t)	I-But(Me3)
27.15	(t)	I-C7/8/9
25.78	(t)	I-C7/8/9
23.05	(t)	I-C7/8/9

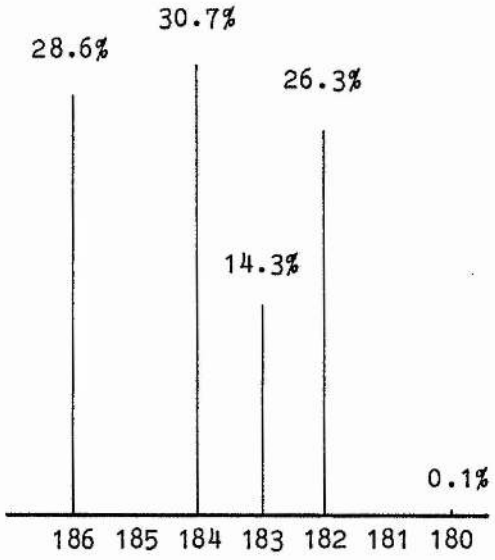
a,b,....,m - Refer to diagrams a),b),....,m) in Appendix 1.
n - Bruker WH360 Spectrometer.
o - Deuterated dichloromethane.
p - Deuterated dimethylsulphoxide.
q - Saturated solution <2.0 M.
(r) - Signal not observed.
(s) - Coupling constant unobtainable.
(t) - Coupling constant not determined.
(u) - 1J(w-c) (Axial) = 163.7 Hz.
(v) - 1J(w-c) (Axial) not observed.
(w) - 1J(w-c) (Equatorial) = 127.6 Hz.
(x) - 1J(w-c) (Equatorial) not observed.

APPENDIX 3

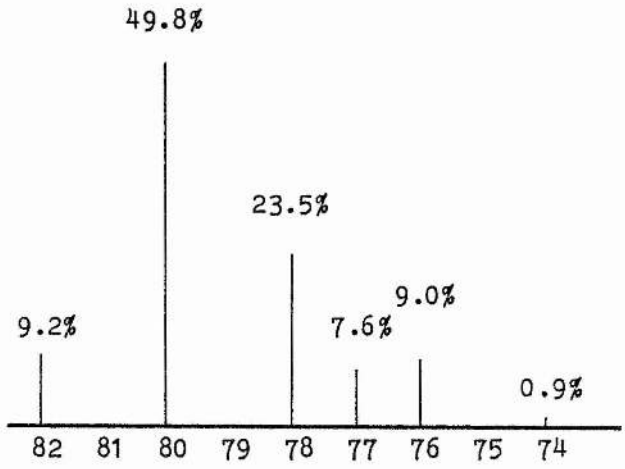
Mass Spectral Data

The ten most intense peaks are listed in order. Additional peaks of interest are listed where appropriate.

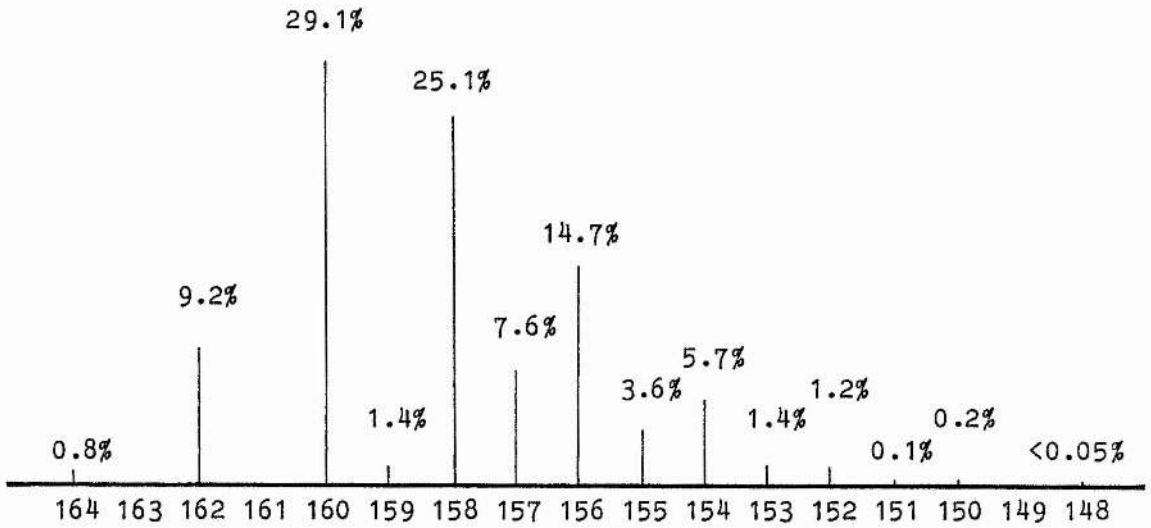
The pattern of peaks arising from one and two selenium atoms, and from one tungsten atom are shown below.



One Tungsten Atom



One Selenium Atom



Two Selenium Atoms

Compound	m/z	RI(%)
(262)		
	59	100.0
	58	100.0
	42	42.2
	121	35.9
	119	28.1
	93	28.1
	80	28.1
	120	25.0
	118	25.0
	43	25.0
	41	25.0
	106	15.6
	92	15.3
	190	9.1
	175	9.1
	160	3.1
	272	0.3

Compound	m/z	RI(%)
(277d)		
	172	100.0
	57	98.1
	187	83.1
	107	69.2
	41	69.2
	106	46.2
	39	34.6
	131	26.9
	85	26.9
	65	22.7
	148	18.1
	205	5.4
	120	5.4

Compound	m/z	RI(%)
(277e)		
	160	100.0
	57	74.0
	118	60.4
	217	58.3
	44	58.3
	41	31.2
	43	27.1
	55	26.0
	117	25.0
	132	22.9
	119	22.9

Compound	m/z	RI(%)
(277f)		
	57	100.0
	213	96.8
	43	65.3
	41	64.2
	55	63.2
	198	56.8
	71	54.7
	69	52.6
	91	44.2
	75	44.2

Compound	m/z	RI(%)
(277g)		
	227	100.0
	57	86.1
	199	52.8
	118	38.9
	41	38.9
	226	33.3
	212	33.3
	147	32.8
	146	26.7
	184	26.1
	170	12.2

Compound	m/z	RI(%)
(280d)		
	173	100.0
	188	68.4
	131	21.1
	174	13.7
	145	10.5
	72	10.0
	130	8.9
	157	8.7
	189	8.3
	144	7.9
	187	6.3

Compound	m/z	RI(%)
(280f)		
	213	100.0
	198	90.0
	212	88.3
	214	40.0
	156	40.0
	199	26.7
	170	26.7
	196	26.0
	182	23.3
	154	22.7
	85	22.7
	171	20.3
	183	19.7
	99	17.0

Compound	m/z	RI(%)
(280g)		
	199	100.0
	227	93.1
	168	74.1
	154	72.4
	184	69.0
	41	55.2
	39	55.2
	170	48.3
	167	44.8
	212	43.1

Compound	m/z	RI(%)
(276b)		
	215	100.0
	200	100.0
	145	65.6
	173	54.0
	44	37.9
	144	31.0
	198	27.6
	131	27.6
	216	21.8
	172	20.7
	157	18.4
	214	17.2
	201	17.2

Compound	m/z	RI(%)
(276c)		
	215	100.0
	200	67.8
	145	46.7
	198	40.0
	173	38.9
	172	38.9
	144	38.9
	216	21.7
	156	20.0
	130	20.0
	214	15.6

Compound	m/z	RI(%)
(276d)		
	215	100.0
	200	100.0
	145	69.0
	44	68.0
	75	58.0
	173	56.0
	144	41.0
	131	38.0
	198	29.0
	172	28.5
	216	21.0
	214	15.0

Compound	m/z	RI(%)
(276f)		
	241	100.0
	44	100.0
	57	81.5
	226	79.6
	55	59.3
	171	55.6
	43	55.6
	199	51.9
	198	48.1
	71	48.1
	41	48.1
	213	22.2
	212	18.5

Compound	m/z	RI(%)
(276g)		
	255	100.0
	212	54.1
	240	42.2
	185	38.4
	213	28.6
	184	28.6
	238	28.1
	57	23.8
	44	22.7
	256	20.0
	254	19.5
	56	12.4
	226	11.9
	198	11.4
	227	10.8
	257	2.2

Compound	m/z	RI(%)
(282a)		
	44	100.0
	40	82.3
	51	35.5
	121	34.7
	39	28.2
	69	28.2
	77	22.6
	283	20.2
	284[a]	18.5
	203	17.7
	204	12.9
	285	11.3
	207	11.3
	282[a]	9.7
	205	8.1
	286[a]	6.5

Compound	m/z	RI(%)
(282b)		
	41	100.0
	45	72.5
	39	70.0
	207	60.3
	125	52.5
	184	50.8
	69	50.0
	159	36.7
	205	33.3
	169	33.3
	51	25.0
	264[a]	22.5

Compound	m/z	RI(%)
(282c)		
	121	100.0
	298[a]	28.8
	39	27.9
	45	27.5
	77	26.7
	69	19.2
	217	18.3
	51	18.3
	44	17.9
	283	15.8
	296[a]	12.5
	297	11.3
	295	10.4
	218	9.6
	294[a]	7.1
	300[a]	6.3
	299	5.8

Compound	m/z	RI(%)
(282d)[b]		
	45	100.0
	167	72.5
	200[b]	57.1
	69	45.0
	39	41.7
	199	27.5
	134	27.5
	248[a]	24.2
	153	17.9
	71	17.5
	91	17.1
	51	17.1
	215	12.1

Compound	m/z	RI(%)
(285a)		
	91	100.0
	236	25.6
	114	22.8
	157	21.7
	41	19.4
	43	18.9
	237[a]	16.9
	234[a]	16.7
	65	15.6
	92	12.8
	39	12.8
	235[a]	12.2
	233[a]	8.9
	144	7.2
	238	6.1
	232	5.6
	239[a]	3.9

b - Contaminated with 4,5-dihydro-3H-[1,2]dithiolo[4,5,1-hi]-[1,2]benzodithiole-7a-S[4] (283d)

Compound	m/z	RI(%)
(285b)		
	44	100.0
	41	61.0
	57	49.2
	43	46.2
	215	39.8
	99	38.1
	200	31.8
	39	31.8
	105	31.4
	77	31.4
	---	---
	279[a]	23.7
	277[a]	15.3
	276[a]	13.6
	264	8.5
	275[a]	6.8
	281[a]	4.2

Compound	m/z	RI(%)
(285c)		
	278	100.0
	279[a]	91.3
	44	82.6
	198	62.0
	276[a]	60.9
	183	58.7
	168	54.3
	184	47.8
	277[a]	45.7
	182	42.4
	---	---
	275[a]	32.6
	280	30.4
	274	19.6
	281[a]	17.4
	264	9.8

Compound	m/z	RI(%)
(288c)		
	170	100.0
	187	95.1
	78	52.2
	105	34.3
	91	32.4
	186	25.9
	157	23.5
	57	21.9
	144	19.5
	77	18.1
	---	---
	131	17.8
	130	17.3
	188	12.4
	201	4.1

Compound	m/z	RI(%)
(285d)		
	279[a]	100.0
	278	91.7
	276[a]	74.1
	198	74.1
	277[a]	73.1
	184	71.3
	183	64.8
	275[a]	63.9
	168	63.9
	182	62.0
	---	---
	280	60.2
	281[a]	39.8
	236	38.9
	274	33.8
	264	32.4

Compound	m/z	RI(%)
(285f)		
	305[a]	100.0
	304	92.2
	302[a]	56.9
	224	52.9
	303[a]	49.0
	306	34.3
	210	33.3
	301[a]	31.4
	209	25.5
	208	22.5
	---	---
	307[a]	20.6
	300	17.6

Compound	m/z	RI(%)
(285g)		
	318	100.0
	319[a]	75.8
	316[a]	58.1
	238	56.5
	57	45.2
	317[a]	40.3
	43	35.5
	41	35.5
	320	30.6
	315[a]	30.6
	56	30.6
	---	---
	314	19.4
	239	19.4
	321[a]	14.5

Compound	m/z	RI(%)
(290a)		
	145	100.0
	144[c]	94.7
	268[c]	68.4
	270	61.1
	266	60.0
	267[c]	33.7
	352[c]	32.6
	354[c]	28.4
	240[c]	28.4
	212[c]	28.4
	296[c]	23.2
	184[c]	23.2
	324[c]	4.7

Compound	m/z	RI(%)
(290b)		
	172	100.0
	186	92.3
	201	76.9
	187[c]	76.9
	268[c]	56.2
	270	53.1
	266	47.7
	145	30.0
	131[c]	30.0
	212[c]	29.2
	352[c]	26.9
	240[c]	26.2
	184[c]	25.4
	157[c]	22.3
	296[c]	20.0
	399[c]	13.8
	324[c]	3.8

Compound	m/z	RI(%)
(290c)		
	268[c]	100.0
	270	95.0
	266[c]	88.0
	212[c]	52.0
	267	50.0
	214[c]	50.0
	240[c]	48.0
	210[c]	47.0
	352[c]	45.0
	242	45.0
	186[c]	42.5
	184[c]	41.0
	201[c]	35.0
	296[c]	32.5
	187	25.0
	172[c]	23.0
	324[c]	8.0

Compound	m/z	RI(%)
(290d)		
	186	100.0
	201[c]	78.0
	268[c]	67.0
	270	60.0
	266	57.0
	187	36.0
	172	36.0
	267[c]	33.0
	212[c]	33.0
	214	30.5
	240[c]	30.0
	352[c]	28.0
	184[c]	27.0
	145[c]	23.0
	296[c]	22.0
	131	14.0
	399[c]	11.0
	324[c]	5.0

Compound	m/z	RI(%)
(290f)		
	227[c]	100.0
	212[c]	81.0
	213	53.3
	226	41.0
	198[c]	32.4
	268[c]	29.5
	270	27.6
	170	27.6
	43	25.7
	266	24.8
	184[c]	16.2
	393[c]	14.8
	352[c]	14.3
	240[c]	13.3
	296[c]	10.5
	450[c]	7.6
	324[c]	2.9

Compound	m/z	RI(%)
(290j)		
	158[c]	100.0
	268[c]	74.5
	270	69.1
	159	67.3
	266	64.5
	144	60.0
	267[c]	38.2
	352[c]	33.6
	212[c]	33.6
	145	32.7
	240[c]	31.8
	44[c]	30.9
	184[c]	25.5
	296[c]	23.6
	324[c]	7.3

Compound	m/z	RI(%)
(293)		
	44	100.0
	137[a]	82.6
	42	59.4
	135[a]	40.6
	133[a]	15.4
	139[a]	13.5
	134[a]	12.8
	93	12.0
	41	10.1
	43	8.3
	122	4.3
	92	4.2
	80	4.1
	57	4.1
	56	4.1

Compound	m/z	RI(%)
(296)		
	145	100.0
	102	36.7
	258[a]	28.8
	146	21.3
	51	16.3
	69	15.4
	256[a]	14.6
	121	14.2
	77	14.2
	210	12.1
	260[a]	7.5
	44	7.5
	255[a]	5.8
	254[a]	5.8

Compound	m/z	RI(%)
(299)		
	43	100.0
	44	16.1
	140	13.7
	39	11.3
	41	8.1
	95	7.3
	69	7.3
	57	7.3
	53	7.3
	45	7.3
	188[a]	1.6
	186[a]	1.1
	185[a]	0.9
	190[a]	0.8
	184[a]	0.7

Compound	m/z	RI(%)
(299)[d]		
	43	100.0
	57	29.1
	108	17.1
	188[a]	16.5
	71	14.9
	39	13.5
	41	12.4
	55	10.7
	65	10.0
	186[a]	8.7
	216[d]	7.3
	184[a]	3.6
	185[a]	3.5
	190[a]	3.3
	217	1.5
	215	1.5

Compound	m/z	RI(%)
(312)[e]		
	91[e]	100.0
	180[e]	84.0
	179	84.0
	268[c]	73.3
	270	65.3
	266	61.3
	178	60.7
	165	44.0
	78	42.0
	212[c]	38.7
	240[c]	36.0
	352[c]	32.0
	184[c]	32.0
	296[c]	25.3
	324[c]	6.7

Compound	m/z	RI(%)
(315a)		
	41	100.0
	40	45.8
	172	30.8
	57	27.5
	44	27.5
	170	26.7
	43	26.2
	39	17.5
	168	16.2
	56	15.0
	236	6.7
	237	4.6
	234	4.2

d - Contaminated with 2,2',6,6'-tetramethyl-4,4'-bipyranylidene (310)
e - Contaminated with 1,1'-bicycloheptatrienylidene (313)

Compound	m/z	RI(%)
(315b)		
	279	100.0
	198	100.0
	278	83.3
	184	68.3
	41	66.7
	276	56.7
	183	56.7
	231	55.8
	36	54.2
	277	53.3
	---	---
	476	2.5
	398	1.2
	318	1.2

Compound	m/z	RI(%)
(315c)		
	278	100.0
	279	95.2
	44	71.4
	276	61.9
	172	61.9
	198	52.4
	170	52.4
	277	47.6
	184	47.6
	226	42.9
	57	42.9
	---	---
	398	33.3
	476	4.8

Compound	m/z	RI(%)
(315d)		
	184	100.0
	172	67.1
	170	61.8
	168	48.7
	183	40.8
	44	40.8
	226	38.2
	279	35.5
	198	35.5
	160	31.6
	---	---
	278	28.9
	57	23.7
	398	3.9
	476	2.0

Compound	m/z	RI(%)
(315f)		
	49	100.0
	252	97.6
	41	97.6
	172	96.0
	170	92.0
	84	80.0
	210	64.0
	251	60.8
	168	50.4
	86	47.2
	---	---
	224	38.4
	238	33.6
	305	25.6
	195	25.6
	182	16.8
	448	8.0
	418	3.6
	476	2.0
	502	0.4

Compound	m/z	RI(%)
(315j)		
	44	100.0
	236	42.6
	156	36.2
	237	29.8
	234	29.8
	57	29.8
	154	27.7
	78	27.7
	198	21.3
	188	21.3
	77	21.3
	55	21.3
	43	21.3
	---	---
	261	11.7
	324	10.6
	339	8.5
	354	2.1

a - Molecular ion peaks arising from selenium isotopes.
b - Contaminated with 4,5-dihydro-3H-[1,2]dithiolo[4,5,1-hi]-[1,2]benzodithiole-7a-S^4 (283d).
c - Contains the tungsten isotope 184.
d - Contaminated with 2,2',6,6'-tetramethyl-4,4'-bipyranylidene (310).
e - Contaminated with 1,1'-bicycloheptatrienylidene (313).

APPENDIX 4

Bibliography

1. U. Schollkopf, Angew. Chem., 1959, 71, 260.
2. S. Trippett, Quart. Rev. Chem. Soc., 1963, 17, 406.
3. S. Trippett, Pure Appl. Chem., 1964, 9, 255.
4. A. Maercker, "Organic Reactions", John Wiley & Sons, 1965, 14, 270.
5. A. Johnson, "Organic Chemistry", Academic Press, 1966, 7, 132.
6. R. L. Reeves, "The Chemistry Of The Carbonyl Group", Interscience, 1966, 1, 570.
7. A. J. Kirby and S. G. Warren, "Reaction Mechanisms In Organic Chemistry", Elsevier, 1967, 5, 184.
8. R. F. Hudson, Chem. Br., 1971, 7, 287.
9. H. O. House, "Modern Synthetic Reactions", 2nd Ed., W. A. Benjamin, 1972, 682.
10. J. I. G. Cadogan, "Organophosphorus Reagents In Organic Synthesis", Academic Press, 1979, 1.
11. I. Gosney and (in part) A. G. Rowley, "Organophosphorus Reagents In Organic Synthesis", Academic Press, 1979, 17.
12. T. W. Campbell, H. G. Walker and G. M. Coppinger, Chem. Rev., 1952, 50, 279.
13. K. W. Bagnall, "The Chemistry Of Selenium, Tellurium And Polonium", Elsevier, 1966, 152.
14. D. S. Breslow and H. Skolnik, "The Chemistry Of Heterocyclic Compounds", Interscience, 1966, 21, 1272.
15. D. H. Reid, Ed., "Organic Compounds Of Sulphur, Selenium And Tellurium", The Chemical Society, 1970, 1.

16. W. H. H. Günther, "Organic Selenium Compounds: Their Chemistry And Biology", Wiley-Interscience, 1973.

17. D. H. Reid, Ed., "Organic Compounds Of Sulphur, Selenium And Tellurium", The Chemical Society, 1973, 2.

18. D. H. Reid, Ed., "Organic Compounds Of Sulphur, Selenium And Tellurium", The Chemical Society, 1975, 3.

19. D. R. Hogg, Ed., "Organic Compounds Of Sulphur, Selenium And Tellurium", The Chemical Society, 1977, 4.

20. D. R. Hogg, Ed., "Organic Compounds Of Sulphur, Selenium And Tellurium", The Chemical Society, 1979, 5.

21. D. R. Hogg, Ed., "Organic Compounds Of Sulphur, Selenium And Tellurium", The Chemical Society, 1981, 6.

22. F. Krafft and W. Vorster, Ber., 1893, 26, 2813.

23. F. Krafft and R. E. Lyons, Ber., 1894, 27, 1761.

24. J. Loevenich, H. Fremdling and M. Föhr, Ber., 1929, 62, 2856.

25. W. H. H. Günther and H. G. Mautner, J. Am. Chem. Soc., 1965, 87, 2708.

26. F. Krafft and R. E. Lyons, Ber., 1894, 27, 1768.

27. F. Zeiser, Ber., 1895, 28, 1670.

28. R. E. Lyons and G. C. Bush, J. Am. Chem. Soc., 1908, 30, 831.

29. D. Hellwinkel and G. Fahrbach, Annalen, 1968, 715, 68.

30. N. N. Yarovenko, V. N. Shemanina and G. B. Gazieva, Zh. Obshch. Khim, 1959, 29, 942; Chem. Abs., 1960, 54, 2158e.

31. N. N. Yarovenko and M. A. Raksha, Zh. Obshch. Khim, 1960, 30, 4064; Chem.Abs., 1961, 55, 20943h.

32. A. Biezais and G. Bergson, Acta Chem. Scand., 1964, 18, 815.

33. C. G. Krespan, J. Am. Chem. Soc., 1961, 83, 3434.

34. E. Bulka and K.-D. Ahlers, Z. Chem., 1963, 3, 348.

35. C. Collard-Charon and M. Renson, Bull. Soc. Chim. Belg., 1962, 71, 531; Chem. Abs., 1963, 58, 6734e.

36. C. Th. Pedersen, Acta Chem. Scand., 1963, 17, 1459.

37. W. J. Franklin and R. L. Werner, Tetrahedron Lett., 1965, 3003.

38. F. Tamboury, Bull. Soc. Chim. Fr., 1903, 29, 761.

39. G. T. Morgan and W. H. Porritt, J. Chem. Soc., 1925, 127, 1755.

40. D. G. Foster, J. Am. Chem. Soc., 1939, 61, 2972.

41. H. J. Backer and J. B. G. Hurenkamp, Recl. Trav. Chim. Pays-Bas, 1942, 61, 802; Chem. Abs., 1944, 38, 3565^2.

42. B. Sjöberg and S. Herdevall, Acta Chem. Scand., 1958, 12, 1347.

43. L. D. Pettit, A. Royston, C. Sherrington and R. J. Whewell, J. Chem. Soc.(B), 1968, 588.

44. E. S. Gould and J. D. McCullough, J. Am. Chem. Soc., 1951, 73, 1109.

45. E. Niwa, H. Aoki, H. Tanaka, K. Munakata and M. Namiki, Chem. Ber., 1966, 99, 3215.

46. Ya. L. Goldfarb, V. P. Litvinov and S. Ozolin, Izv. Akad. Nauk. SSSR, Ser. Khim., 1968, 6, 1419; Chem. Abs., 1968, 69, 96522v.

47. L. Brandsma, H. E. Wijers and J. F. Arens, Recl. Trav. Chim. Pays-Bas, 1962, 81, 583.

48. L. Brandsma, H. E. Wijers and C. Jonker, Recl. Trav. Chim. Pays-Bas, 1964, 83, 208.

49. A. A. Petrov, S. I. Radchenko, K. S. Mingaleva, I. G. Savich and V. B. Lebedev, Zh. Obshch. Khim., 1964, 34, 1899; Chem. Abs., 1964, 61, 8179g.

50. Yu. A. Boiko, B. S. Kupin and A. A. Petrov, Zh. Org. Khim., 1968, 4, 1355; Chem. Abs., 1968, 69, 86544q.

51. J. Gosselck and E. Wolters, Z. Naturforsch., 1962, 17, 131; Chem. Abs., 1962, 57, 4582e.

52. J. Ashby, L. A. Cort, J. A. Elvidge and U. Eisner, J. Chem. Soc.(C), 1968, 2311.

53. R. F. Curtis, S. N. Hasnain and J. A. Taylor, J. Chem. Soc., Chem. Commun., 1968, 365.

54. M. Renson and R. Collienne, Bull. Soc. Chim. Belg., 1964, 73, 419; Chem. Abs., 1964, 61, 10645d.

55. F. Zetzsche and H. Pinske, Ber., 1941, 74, 1022.

56. R. A. Zingaro, F. C. Bennett, Jr. and G. W. Hammar, J. Org. Chem., 1953, 18, 292.

57. F. von Dechend, Ber., 1874, 7, 1273.

58. G. Hofmann, Annalen, 1889, 250, 294.

59. W. Becker, Ber., 1904, 37, 2550.

60. K. Kindler, Annalen, 1923, 431, 187.

61. L. G. S. Brooker, G. H. Keyes and F. L. White, J. Am. Chem. Soc., 1935, 57, 2492.

62. H. J. Backer and H. Bos, Recl. Trav. Chim. Pays-Bas, 1943, 62, 580; Chem. Abs., 1945, 39, 3531^{3}.

63. R. E. Dunbar and E. P. Painter, J. Am. Chem. Soc., 1947, 69, 1833.

64. L. C. King and R. J. Hlavacek, J. Am. Chem. Soc., 1951, 73, 1864.

65. K. A. Jensen, M. Due, A. Holm and C. Wentrup, Acta Chem. Scand., 1966, 20, 2091.

66. D. S. Margolis and R. W. Pittman, J. Chem. Soc., 1957, 799.

67. G. A. Heath, R. L. Martin and I. M. Stewart, Aust. J. Chem., 1969, 22, 83.

68. M. G. Jackson, Ph.D. Thesis, University of St. Andrews, 1973.

69. W. H. H. Günther, "Organic Selenium Compounds: Their Chemistry And Biology", Wiley-Interscience, 1973, 40.

70. W. Klemm, H. Sodomann and P. Langmesser, Z. Anorg. Allg. Chem., 1939, 241, 281.

71. L. Brandsma and H. E. Wijers, Recl. Trav. Chim. Pays-Bas, 1963, 82, 68.

72. D. L. Klayman and T. S. Griffin, J. Am. Chem. Soc., 1973, 95, 197.

73. D. H. Reid and R. G. Webster, J. C. S. Perkin Trans. 1, 1975, 775.

74. D. H. Reid, R. G. Webster and (in part) S. McKenzie, J. C. S. Perkin Trans. 1, 1979, 2334.

75. J. G. Dingwall, S. McKenzie and D. H. Reid, J. Chem. Soc.(C), 1968, 2543.

76. G. R. Waitkins and R. Shutt, Inorg. Synth., 1946, 2, 186; Chem. Abs., 1946, 40, 7028[1].

77. M. Giua and R. Bianco, Gazz. Chim. Ital., 1959, 89, 693; Chem. Abs., 1960, 54, 22454c.

78. W. Muthmann and E. Schröder, Ber., 1900, 33, 1765.

79. H. Rheinboldt and H. V. de Campos, J. Am. Chem. Soc., 1950, 72, 2784.

80. T. Tarantelli and C. Pecile, Ann. Chim.(Rome), 1962, 52, 75; Chem. Abs., 1962, 57, 710g.

81. J. Goerdeler, D. Gross and H. Klinke, Chem. Ber., 1963, 96, 1289.

82. F. Challenger, A. T. Peters and J. Halevy, J. Chem. Soc., 1926, 1648.

83. T. W. Campbell and M. T. Rogers, J. Am. Chem. Soc., 1948, 70, 1029.

84. H. P. Kaufmann and F. Kögler, Ber., 1926, 59, 178.

85. L.-B. Agenäs, Acta Chem. Scand., 1963, 17, 268.

86. L.-B. Agenäs, Ark. Kemi, 1969, 30, 417.

87. L.-B. Agenäs and B. Lindgren, Ark. Kemi, 1968, 28, 145.

88. L.-B. Agenäs, Ark. Kemi, 1965, 23, 145.

89. L.-B. Agenäs, Ark. Kemi, 1965, 23, 155.

90. M. V. Kudchadker, R. A. Zingaro and K. J. Irgolic, Can. J. Chem., 1968, 46, 1415.

91. N. I. Zemlyanskii and R. D. Gorak, Zh. Obshch. Khim., 1971, 41, 1691; Chem. Abs., 1972, 76, 3497x.

92. N. I. Zemlyanskii and R. D. Gorak, Zh. Obshch. Khim., 1971, 41, 2446; Chem. Abs., 1972, 76, 112602y.

93. R. D. Gorak, N. I. Zemlyanskii and I. V. Murav'ev, Zh. Obshch. Khim., 1972, 42, 56; Chem. Abs., 1972, 77, 100644w.

94. N. I. Zemlyanskii, R. D. Gorak and Ya. I. Kolodii, Ukr. Khim. Zh., 1973, 39, 68; Chem. Abs., 1973, 78, 110749u.

95. M. I. Ivanyutin, Org. Reagenty Anal. Khim., 1973, 44; Chem. Abs., 1975, 83, 9103g.

96. H. Behrens and G. Haschka, Chem. Ber., 1961, 94, 1191.

97. R. G. Melton and R. A. Zingaro, Can. J. Chem., 1968, 46, 1425.

98. J. H. van den Hende and E. Klingsberg, J. Am. Chem. Soc., 1966, 88, 5045.

99. German Patent, 1954, 910,199; Chem. Abs., 1959, 53, 936h.

100. K. Geisler, H. Below, A. Möller and E. Bulka, Z. Chem., 1984, 24, 99.

101. C. Collard-Charon and M. Renson, Bull. Soc. Chim. Belg., 1963, 72, 304; Chem. Abs., 1963, 59, 8271b.

102. K. A. Jensen and P. H. Nielsen, Acta Chem. Scand., 1966, 20, 597.

103. I. D. Rae and M. J. Wade, Int. J. Sulphur Chem., 1973, 8, 519.

104. K. A. Jensen, G. Felbert and B. Kagi, Acta Chem. Scand., 1966, 20, 281.

105. H. E. Hallam and C. M. Jones, J. Chem. Soc.(A), 1969, 1033.

106. R. Stolle and L. Gutmann, J. Prakt. Chem., 1904, 69, 509.

107. C. D. Mickey and R. A. Zingaro, Int. J. Sulphur Chem., 1973, 8, 557.

108. K. Burger and R. Ottlinger, Synthesis, 1978, 44.

109. J. F. K. Wilshire, Aust. J. Chem., 967, 20, 359.

110. K. B. Wiberg and S. D. Nielsen, J. Org. Chem., 1964, 29, 3353.

111. D. H. Olson, Tetrahedron Lett., 1966, 2053.

112. J. P. Schaefer, B. Horvath and H. P. Klein, J. Org. Chem., 1968, 33, 2647.

113. D. Paquer, M. Perrier and J. Vialle, Bull. Soc. Chim. Fr., 1970, 4517.

114. M. Perrier and J. Vialle, Bull. Soc. Chim. Fr., 1971, 4591.

115. M. Perrier and J. Vialle, Bull. Soc. Chim. Fr. II, 1979,199.

116. F. E. King and D. G. I. Felton, J. Chem. Soc., 1949, 274.

117. M. Perrier and J. Vialle, Bull. Soc. Chim. Fr. II, 1979,205.

118. H. Meier and E. Voigt, Tetrahedron, 1972, 28, 187.

119. J. Neve, M. Hanocq and L. Molle, Talanta, 1979, 26, 15; Chem. Abs., 1979, 91, 19582s.

120. J. Neve, M. Hanocq and L. Molle, Mikrochim. Acta, 1980, 1, 41.

121. E. P. Painter, Chem. Rev., 1941, 28, 179.

122. H. E. Ganther, Biochemistry, 1968, 7, 2898; Chem. Abs., 1968, 69, 57010g.

123. K. Dostal, P. Mosna and Z. Zak, Z. Chem., 1966, 6, 153.

124. F. Foerster, F. Lange, O. Drossbach and W. Seidel, Z. Anorg. Allg. Chem., 1923, 128, 245.

125. D. L. Klayman, J. Org. Chem., 1965, 2454.

126. D. H. Reid, J. Chem. Soc.(C), 1971, 3187.

127. K. Gleu and R. Schaarschmidt, Ber., 1939, 72, 1246.

128. J. Czyzewski and D. H. Reid, J. C. S. Perkin Trans. 1, 1983, 777.

129. G. Calcagni, Gazz. Chim. Ital., 1923, 53, 114; Chem. Abs., 1923, 17, 2378.

130. E. Schulek and E. Körös, J. Inorg. Nucl. Chem., 1960, 13, 58.

131. L. Tschugaeff and W. Chlopin, Ber., 1914, 47, 1269.

132. M. L. Bird and F. Challenger, J. Chem. Soc., 1942, 570.

133. A. Fredga, Acta Chem. Scand., 1963, 17, S51.

134. W. H. H. Günther, J. Org. Chem., 1967, 32, 3929.

135. D. M. Yost and C. E. Kircher, J. Am. Chem. Soc., 1930, 52, 4680.

136. H. Brintzinger, K. Pfannstiel and H. Vogel, Z. Anorg. Allg. Chem., 1948, 256, 75; Chem. Abs., 1949, 43, 2159e.

137. N. W. Tideswell and J. D. McCullough, J. Am. Chem. Soc., 1956, 78, 3026.

138. N. Katsaros and J. W. George, J. Chem. Soc., Chem. Commun., 1968, 662.

139. F. Lautenschlaeger, J. Org. Chem., 1969, 34, 4002.

140. H. W. Bausor, C. S. Gibson and W. J. Pope, J. Chem. Soc., 1920, 117, 1453.

141. C. E. Boord and F. F. Cope, J. Am. Chem. Soc., 1922, 44, 395.

142. N. N. Yarovenko, M. A. Raksha and V. N. Shemanina, Zh. Obshch. Khim., 1960, 30, 4069; Chem. Abs., 1961, 55, 20942f.

143. R. F. Riley, J. Flato and D. Bengels, J. Org. Chem., 1962, 27, 2651.

144. H. Funk and W. Papenroth, J. Prakt. Chem., 1958, 8, 256; Chem. Abs., 1960, 54, 1284f.

145. A. Michaelis and Fr. Kunckell, Ber., 1897, 30, 2823.

146. Fr. Kunckell and R. Zimmermann, Annalen, 1901, 314, 281.

147. R. E. Nelson and R. N. Jones, J. Am. Chem. Soc., 1930, 52, 1588.

148. S. Patai, M. Sokolovsky and A. Friedlander, Proc. Chem. Soc., 1960, 181.

149. S.-H. Chu and H. G. Mautner, J. Org. Chem., 1962, 27, 2899.

150. E. P. Painter, J. Am. Chem. Soc., 1947, 69, 229.

151. G. Zdansky, Ark. Kemi, 1960, 17, 273; Chem. Abs., 1962, 56, 10263d.

152. L.-B. Agenäs, Ark. Kemi, 1965, 23, 463.

153. L.-B. Agenäs, Ark. Kemi, 1965, 24, 415.

154. L.-B. Agenäs and B. Persson, Acta Chem. Scand., 1967, 21, 835.

155. L.-B. Agenäs and B. Persson, Acta Chem. Scand., 1967, 21, 837.

156. D. Theodoropoulos, I. L. Schwartz and R. Walter, Tetrahedron Lett., 1967, 2411.

157. C. S. Pande, J. Rudick and R. Walter, J. Org. Chem., 1970, 35, 1440.

158. H. G. Grimm and H. Metzger, Ber., 1936, 69, 1356.

159. D. J. G. Ives, R. W. Pittman and W. Wardlaw, J. Chem. Soc., 1947, 1080.

160. D. Barnard and D. T. Woodbridge, J. Chem. Soc., 1961, 2922.

161. K. A. Jensen, Quart. Rept. Sulphur Chem., 1970, 5, 45.

162. N. N. Yarovenko, G. B. Gazieva, V. N. Shemanina and N. A. Fedorova, Zh. Obshch. Khim., 1959, 29, 940; Chem. Abs., 1959, 53, 21346i.

163. S. Larsen and L. Henriksen, Acta Chem. Scand., 1984, 38A, 289.

164. R. A. Cherkasov, G. A. Kutyrev and A. N. Pudovik, Tetrahedron, 1985, 41, 2568.

165. S. Oae, A. Nakanishi and N. Tsujimoto, Chem. Ind., 1972, 575.

166. J. Perregaard, I. Thomsen and S.-O. Lawesson, Bull. Soc. Chim. Belg., 1977, 86, 321; Chem. Abs., 1977, 87, 134368f.

167. J. Perregaard, B. S. Pedersen and S.-O. Lawesson, Acta Chem. Scand., 1977, 31B, 460.

168. G. Ottmann and H. Hooks, Jr., Angew. Chem., Int. Ed. Engl., 1966, 5, 725.

169. C. Eaborn, J. Chem. Soc., 1950, 3077.

170. G. A. Kutyrev, A. A. Kutyrev, R. A. Cherkasov and A. N. Pudovik, Dokl. Akad. Nauk. SSSR, 1979, 247, 616; Chem. Abs., 1980, 92, 58851u.

171. B. S. Pedersen and S.-O. Lawesson, Bull. Soc. Chim. Belg., 1977, 86, 693; Chem. Abs., 1978, 88, 61735g.

172. T. N. Chan and J. R. Finkenbine, J. Am. Chem. Soc., 1972, 94, 2880.

173. F. N. Mazitova and V. K. Khairullin, Zh. Obshch. Khim., 1981, 51, 958; Chem. Abs., 1981, 95, 81127h.

174. B. S. Pedersen, S. Scheibye, N. H. Nilsson and S.-O. Lawesson, Bull. Soc. Chim. Belg., 1978, 87, 223; Chem. Abs., 1978, 89, 128559u.

175. K. A. Jørgensen, M. T. M. El-Wassimy and S.-O. Lawesson, Synthesis, 1983, 373.

176. S. Scheibye, R. Shabana, S.-O. Lawesson and C. Rømming, Tetrahedron, 1982, 38, 993.

177. S. Shabana, J. B. Rasmussen, S.-O. Olesen and S.-O. Lawesson, Tetrahedron, 1980, 36, 3047.

178. J. B. Rasmussen, R. Shabana and S.-O. Lawesson, Tetrahedron, 1981, 37, 197.

179. B. S. Pedersen, S. Scheibye, K. Clausen and S.-O. Lawesson, Bull. Soc. Chim. Belg., 1978, 87, 293; Chem. Abs., 1978, 89, 109786z.

180. S. Scheibye, B. S. Pedersen and S.-O. Lawesson, Bull. Soc. Chim. Belg., 1978, 87, 229; Chem. Abs., 1978, 89, 108050t.

181. M. P. Cava and M. I. Levinson, Tetrahedron, 1985, 41, 5061.

182. E. Klingsberg, Quart. Rev., 1969, 23, 537.

183. D. H. Reid, "Organic Compounds Of Sulphur, Selenium And Tellurium", The Chemical Society, 1970, 1, 321.

184. N. Lozac'h, "Advances In Heterocyclic Chemistry", Academic Press, 1971, 13, 161.

185. R. J. S. Beer, "Organic Compounds Of Sulphur, Selenium And Tellurium", The Chemical Society, 1973, 2, 497.

186. R. J. S. Beer, "Organic Compounds Of Sulphur, Selenium And Tellurium", The Chemical Society, 1975, 3, 494.

187. R. J. S. Beer, "Organic Compounds Of Sulphur, Selenium And Tellurium", The Chemical Society, 1977, 4, 300.

188. R. Gleiter and R. Gygax, Top. Curr. Chem., 1976, 63, 49.

189. D. Leaver, "Organic Compounds Of Sulphur, Selenium And Tellurium", The Chemical Society, 1979, 5, 310.

190. C. Th. Pedersen, Sulphur Reports, 1980, 1, 18.

191. M. Davis, "Organic Compounds Of Sulphur, Selenium And Tellurium", The Chemical Society, 1981, 6, 299.

192. A. Hordvik and K. Julshamn, Acta Chem. Scand., 1971, 25, 2507.

193. L. Pauling, "The Nature Of The Chemical Bond", 3rd Ed., Cornell University Press, 1960.

194. D. W. Cruickshank, Acta Crystallogr., 1957, 10, 504.

195. A. Hordvik and J. A. Porten, Acta Chem. Scand., 1973, 27, 485.

196. F. A. Amundsen, L. K. Hansen and A. Hordvik, Acta Chem. Scand., 1982, 36A, 673.

197. R. Gleiter and R. Hoffmann, Tetrahedron, 1968, 24, 5899.

198. A. Hordvik and K. Julshamn, Acta Chem. Scand., 1971, 25, 1895.

199. A. Hordvik, T. S. Rimala and L. J. Saethre, Acta Chem. Scand., 1973, 27, 360.

200. A. Hordvik, T. S. Rimala and L. J. Saethre, Acta Chem. Scand., 1972, 26, 2139.

201. A. Hordvik, Acta Chem. Scand., 1971, 25, 1583.

202. L. K. Hansen, A. Hordvik and L. J. Saethre, J. Chem. Soc., Chem. Commum., 1972, 222.

203. A. Hordvik, Acta Chem. Scand., 1966, 20, 1885.

204. A. Hordvik, E. Sletten and J. Sletten, Acta Chem. Scand., 1969, 23, 1852.

205. E. C. Llaguno and I. C. Paul, J. C. S. Perkin Trans. 2, 1972, 2001.

206. R. G. Webster, Ph.D. Thesis, University of St.Andrews, 1973.

207. J. G. Dingwall, A. R. Dunn, D. H. Reid and K. O. Wade, J. C. S. Perkin Trans. 1, 1972, 1360.

208. R. M. Christie and D. H. Reid, J. C. S. Perkin Trans. 1, 1976, 228.

209. M. Perrier, R. Pinel and J. Vialle, J. Heterocycl. Chem., 1975, 12, 639.

210. J. Møller, R. M. Christie, C. Th. Pedersen and D. H. Reid, Acta Chem. Scand., 1976, 30B, 600.

211. Y. Mollier, F. Terrier and N. Lozac'h, Bull. Soc. Chim. Fr., 1964, 1778.

212. R. Pinel, Y. Mollier and N. Lozac'h, Bull. Soc. Chim. Fr., 1966, 1049.

213. L. J. Saethre, N. Martensson, S. Svensson, P. A. Malmquist, U. Gelius and K. Siegbahn, J. Am. Chem. Soc., 1980, 102, 1783.

214. D. T. Clark, D. Kilcast and D. H. Reid, J. Chem. Soc., Chem. Commum., 1971, 638.

215. D. T. Clark, Int. J. Sulphur Chem., 1972, 7C, 11.

216. B. J. Lindberg, Int. J. Sulphur Chem., 1972, 7C, 33.

217. G. Pfister-Guillouzo and N. Lozac'h, Bull. Soc. Chim. Fr., 1963, 153.

218. J. Bignebat and H. Quiniou, Compt. Rendus, 1968, 267C, 180.

219. J. Bignebat and H. Quiniou, Compt. Rendus, 1969, 269C, 1129.

220. J. G. Dingwall, D. H. Reid and K. Wade, J. Chem. Soc.(C), 1969, 913.

221. R. J. S. Beer, D. Cartwright, R. J. Gait and D. Harris, J. Chem. Soc.(C), 1971, 963.

222. G. Duguay, D. H. Reid, K. O. Wade and (in part) R. G. Webster, J. Chem. Soc.(C), 1971, 2829.

223. R. M. Christie, A. S. Ingram, D. H. Reid and R. G. Webster, J. C. S. Perkin Trans. 1, 1974, 722.

224. R. M. Christie and D. H. Reid, J. C. S. Perkin Trans. 1, 1977, 848.

225. D. H. Reid and R. G. Webster, J. C. S. Perkin Trans. 1, 1977, 854.

226. S. Bezzi, C. Garbuglio, M. Mammi and G. Traverso, Gazz. Chim. Ital., 1958, 88, 1226; Chem. Abs., 1959, 53, 22007g.

227. S. Bezzi, M. Mammi and C. Garbuglio, Nature, 1958, 182, 247.

228. G. Giacometti, G. Rigatti, J. Chem. Phys., 1959, 30, 1633; Chem. Abs., 1959, 53, 19556i.

229. K. Maeda, Bull. Soc. Chim. Jpn., 1960, 33, 1466; Chem. Abs., 1961, 55, 14055i.

230. K. Maeda, Bull. Soc. Chim. Jpn., 1961, 34, 785; Chem. Abs., 1962, 56, 105i.

231. K. Maeda, Bull. Soc. Chim. Jpn., 1961, 34, 1166; Chem. Abs., 1962, 56, 5531d.

232. R. A. W. Johnstone and S. D. Ward, Theor. Chim. Acta, 1969, 14, 420.

233. M. H. Palmer and R. H. Findlay, Tetrahedron Lett., 1972, 4165.

234. M. H. Palmer and R. H. Findlay, J. C. S. Perkin Trans. 2, 1974, 1885.

235. M. H. Palmer and R. H. Findlay, J. Mol. Struct., 1977, 37, 229; Chem. Abs., 1977, 87, 5202y.

236. R. Daudel and O. Chalvet, J. Chim. Phys., 1956, 53, 943; Chem. Abs., 1957, 51, 6295a.

237. R. J. Hach and R. E. Rundle, J. Am. Chem. Soc., 1951, 73, 4321.

238. O. Andresen and C. Rømming, Acta Chem. Scand., 1962, 16, 1882.

239. O. Foss and S. Hague, Acta Chem. Scand., 1963, 17, 1807.

240. T. Migchelsen and A. Vos, Acta Crystallogr., 1967, 23, 796.

241. T. Bernstein and F. H. Herbstein, Acta Crystallogr., 1968, 324, 1640.

242. S. L. Lawton and R. A. Jacobson, Inorg. Chem., 1968, 7, 2124.

243. J. I. Musher, Angew. Chem., Int. Ed. Engl., 1969, 8, 54.

244. S. Hague, Acta Chem. Scand., 1971, 25, 1134.

245. G. Traverso, Ann. Chim. Ital. 1957, 47, 3.

246. J. Czyzewski, Ph.D. Thesis, University of St.Andrews, 1977.

247. D. H. Reid and R. G. Webster, J. C. S. Perkin Trans. 1, 1975, 2097.

248. S. McKenzie and D. H. Reid, J. Chem. Soc.(C), 1970, 145.

249. R. G. Webster, M.Sc. Thesis, University of St.Andrews, 1971.

250. D. H. Reid, Unpublished results.

251. D. Brunt, Unpublished results.

252. R. G. Pearson and J. Songstad, J. Am. Chem. Soc., 1969, 89, 1827.

253. W. J. Stec, T. Sudol and B. Uznanski, J. Chem. Soc., Chem. Commun., 1975, 467.

254. A. M. McRoberts, Ph.D. Thesis, University of St. Andrews, 1984.

255. D. O. Holland and J. H. C. Nayler, J. Chem. Soc., 1955, 1657.

256. J. G. Dingwall, D. H. Reid and J. D. Symon, J. Chem. Soc.(C), 1970, 2412.

257. W. Kirmse, "Organic Chemistry", 2nd Ed., Academic Press, 1971, 1, 65.

258. P. J. Pogorzelec and D. H. Reid, J. Chem. Soc., Chem. Commun., 1983, 289.

259. C. J. Pouchert, "The Aldrich Library Of NMR Spectra", 2nd Ed., Aldrich Chemical Co. Inc., 1983, 1.

260. L. Henriksen, Synthesis, 1974, 501.

261. N. Plavac, I. W. J. Still, M. S. Chauhan and D. M. McKinnon, Can. J. Chem., 1975, 53, 836.

262. H. Spies, K. Gewald and R. Mayer, J. Prakt. Chem., 1971, 313, 804; Chem. Abs., 1972, 76, 85731f.

263. D. H. Reid, J. Chem. Soc.(C), 1971, 3187.

264. G. C. Levy, R. L. Lichter and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd Ed., J. Wiley & Sons, 1980, 119.

265. R. Willstätter and T. Wirth, Ber., 1909, 42, 1920.

266. G. R. Pettit and L. R. Garson, Can. J, Chem., 1965, 43, 2640.

267. E. Klingsberg, J. Am. Chem. Soc., 1961, 83, 2934.

268. A. G. Briggs, M.Sc. Thesis, University of St. Andrews, 1977.

269. A. Thuillier and J. Vialle, Bull. Soc. Chim. Fr., 1962, 2187.

270. E. W. Abel, I. S. Butler and J. G. Reid, J. Chem. Soc., 1963, 2068.

271. M. Fraser, A. Melera, B. B. Molloy and D. H. Reid, J. Chem. Soc., 1962, 3288.

272. A. R. Butler and C. Glidewell, J. Chem. Research, 1982, (S) 65, (M) 0801.